THE OHIO JOURNAL OF SCIENCE

VOL. LIII SEPTEMBER, 1953 No. 5

THE TRAPPING OF SOLAR ENERGY

A symposium presented to the Chemistry Section at the annual meeting of the Ohio Academy of Science held at Kent State University, Kent, Ohio, April 18, 1952.

Chairman: EDWARD M. REDDING.
Honorary Chairman: CHARLES F. KETTERING.
Participants: JOHN H. SHAW, GEORGE O. G. LÖF, THOMAS D. NEVENS, PAUL ROTHEMUND, JACK G. CALVERT, DAN TRIVICH, J. ALLEN HYNEK.
Symposium Editor: WILLIAM M. MACNEVIN.

INTRODUCTION

WILLIAM M. MACNEVIN
Department of Chemistry, The Ohio State University, Columbus 10

There is a conviction among scientists that man can improve upon the efficiency with which nature converts sunlight to chemical energy through photosynthesis. On the occasion of the 75th anniversary of the founding of the American Chemical Society, President Conant of Harvard predicted that in another 50 years, man would be using the sun as a practical source of energy.

When we step outdoors on a sunny summer day we are aware of two sensations, heat and light. Part of the sun's energy reaches us as longer wave-length or "red" waves which supply heat. Part reaches us as shorter wave-length or light waves. Both kinds of waves represent energy and it is with the principles involved in trapping of this energy either directly as heat energy or indirectly by converting it to chemical or electrical energy that the following papers are directed. Conversion to chemical energy also includes photosynthesis in plants, an area of vital interest to agriculture.

The magnitude of solar energy is indicated by two practical statements. The energy striking the roof of an average house in one-half hour on a sunny summer day is enough to supply that house with heat and light and utilities for a whole year. The second statement is that it would take 2 million atomic bombs (fission type) to produce energy equivalent to the solar energy striking the United States in one day.

Energy from solar sources as it reaches the earth is diffuse in contrast to atomic energy. Atomic energy is already trapped and only needs release. Atomic energy may be obtained in a high degree of intensity and therefore have special uses. Solar energy in its diffuse state must first be trapped. Some device which will "filter" it from the atmosphere must be designed. Such a device must also be adaptable to concentration of the energy in order to give it a potential necessary

for its adaptation to modern industry. There is no reason at present why concentration of energy once derived from solar sources, sufficient to supply the demands of modern industry cannot be achieved.

The storage of energy from solar sources presents a special problem. It would be inconvenient if the energy were available only during daylight. This problem is not insurmountable and has been solved in several ways already. Sugar represents stored solar energy perhaps in its most convenient form. Solar energy may also be stored by absorbing it as heat of dehydration of such substances as Glauber's salt. Solar energy has also been stored as water raised during daylight hours by sun-fired steam pumps. The storing of electrical power derived from solar energy has the same limitations as hydroelectric power.

The primary problem therefore is the trapping of solar energy, that is, the conversion of the energy of light waves to other forms of energy, particularly chemical and electrical energy. When we know how this process works, we will have a sound basis for studying the factors that affect its efficiency and thus in time make the use of solar energy practical.

In the following papers, the authors have attempted to state the scientific principles involved in the various ways of trapping solar energy, the factors that affect the efficiency and some of the accomplishments already achieved.

SOLAR RADIATION

JOHN H. SHAW

Department of Physics and Astronomy, The Ohio State University, Columbus 10

This paper is an introduction to a discussion of methods of converting part of the enormous flux of solar radiation incident on the surface of the earth directly into useful energy. Until now, the human race has been content to watch natural processes change solar radiation into other forms of energy and to rely on these secondary sources for most of the power it requires. For example, the energy derived from food, coal, gasoline and other petroleum products, and electricity generated in hydroelectric power plants, was all obtained from sunlight. At present a large fraction of our energy comes from coal and oil which were produced very slowly. As we are using these stocks of energy many times faster than they are being replaced, it is becoming increasingly urgent for us to develop methods of drawing upon our current supply of solar energy for the power we need. Thus, we need to know whether it is sufficient to rely on natural processes for converting solar energy or whether it is possible to devise ways of converting solar energy directly and economically into useful power. Although this problem has been considered for many years, no method has yet been invented which can compete with present sources of power. The problem is complicated by the nature of solar radiation which is very different from any other source of power so far used. This introduction is intended to discuss the nature of solar radiation, the amount of energy available, and the amount which we can hope to convert into useful energy using presently known methods. The description of the various methods proposed is discussed by other authors.

THE NATURE OF SOLAR RADIATION

When we step out of the shade on a summer's day we are conscious of being warmed by sunlight. What does sunlight consist of and how was it formed?

THE OHIO JOURNAL OF SCIENCE 53 (5): 258, September, 1953.

Part of the radiation from the sun is in the form of visible light which, when passed through a prism, produces a spectrum containing all the pure colors from red at one end to violet at the other. Each color in the spectrum is due to a particular type of radiation and the different colors are caused by radiation of different wave-lengths. Light is a form of electromagnetic radiation of the same nature as radio signals and consists of a rapidly alternating electromagnetic field. The product of the number of oscillations of the field per second and the wave-

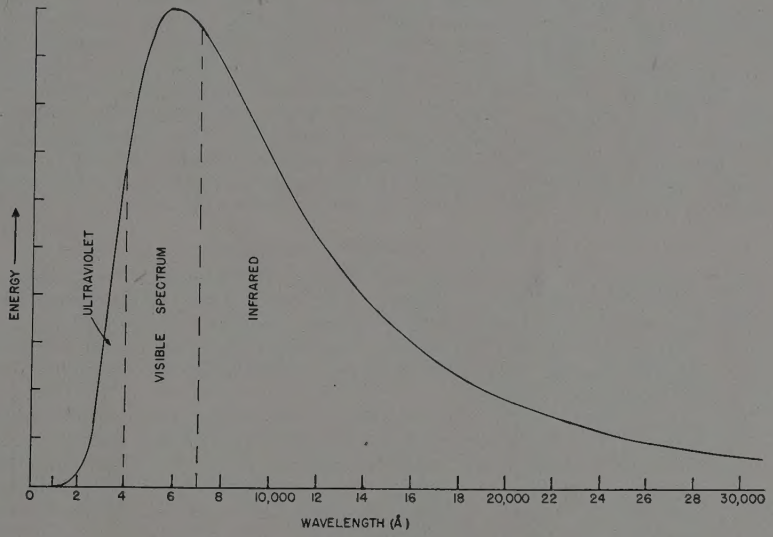


FIGURE 1. The spectral distribution of energy leaving the sun.

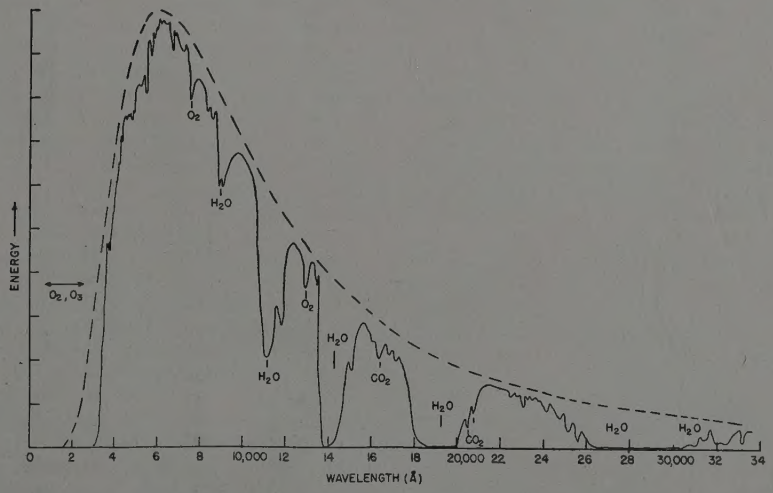


FIGURE 2. Spectral distribution of sunlight arriving at earth's surface.

length gives the velocity of the radiation. In free space this velocity is 186,000 mi./sec. for all wavelengths. The violet end of the spectrum corresponds to radiation of wavelengths about 4,000 Ångstroms (1 Ångstrom = 10^{-8} cm.), and the red end to a wavelength of about 8,000 Ångstroms. In addition, the sun also emits radiation of shorter wavelength than the violet end of the visible spectrum, called ultraviolet radiation. Beyond the red end is infrared radiation.

If the amount of energy present at each wavelength is measured, a curve can be drawn showing the energy distribution of solar radiation. This curve, shown in figure 1, has a maximum near the green region of the visible spectrum (5,000 Å.). When the solar spectrum is investigated with a spectrometer, an instrument which enables the spectrum to be examined in detail, narrow absorption lines are found throughout the whole spectrum where the energy at certain wavelengths is greatly reduced. In some cases the absorption takes place in the solar atmosphere and in others in the earth's atmosphere. Measurements made at ground level show the solar energy disappears entirely at some places in both the ultraviolet and infrared regions, due to complete absorption by the earth's atmosphere (fig. 2).

THE SUN

The temperature of the solar surface emitting radiation can be determined from the spectral distribution of sunlight. The shape of the energy curve and the wavelength position of maximum energy indicate that this temperature is about 6,000° C. To understand how the surface continues to keep so hot when it is continually radiating energy into space requires a knowledge of the physical and chemical states existing in the sun.

The sun is a great ball of intensely hot matter which, because it is so hot, must be gaseous. Its visible surface is 864,000 miles in diameter and, in volume, the sun is one and a third million times as large as the earth. Surrounding the sun is an extremely tenuous atmosphere which is usually only visible during an eclipse. The average density of the sun is about 1.4 times that of water and its mean distance from the earth is 93 million miles.

The energy given off by the sun is generated in its interior. Because this lies below the visible surface it is not directly observable, however, the temperature must increase from the 6,000° C. at the surface, to many times this value at the center. This increase is due, in part, to the gravitational forces holding the sun together, since, as the center of the sun is approached, the weight of the overlying layers increases and both the density and the temperature of the lower layers must increase to support the weight. At the center, the density is probably close to 80 times that of water and the temperature around 40 million degrees C. These high temperatures and pressures enable nuclear reactions to occur which furnish sufficient energy to keep the sun at its high temperature.

Various types of nuclear reactions have been suggested, but it is now believed that the most important one is a chain of processes in which carbon nuclei react with protons (hydrogen nuclei) to build up more complex atoms which are later decomposed to form carbon atoms again and helium nuclei. The net result of this reaction is that four protons combine to form one helium nucleus. Since the mass of the resulting helium nucleus is less than that of the four protons, mass is lost in the reaction. It is converted into radiation, following Einstein's law which states that $E = mc^2$, where m is the mass which has disappeared, c is the velocity of light and E is the energy of the radiation.

Unlike earlier ideas of the origin of the sun's energy—such as, the heat produced by chemical reactions or by the gradual contraction of the sun—the theory that mass is being converted into energy is the only one yet advanced which will, working on reasonable assumptions, account for the huge amount of radiation the sun must have emitted since its birth more than a billion years ago. From

the size of the sun's surface and its temperature it is possible to calculate that mass is being converted into energy at the colossal rate of 4 million tons per second; however there is still sufficient hydrogen present for the sun to keep on emitting energy, on its present scale, for many more millions of years.

The energy produced in the interior of the sun has to find its way to the surface before it can escape into space. The normal methods of conduction or convection of heat are not rapid enough to transport the enormous amount of energy from the interior to the surface. Instead, it is believed that energy is brought to the surface by radiative processes. The atoms in the interior of the sun emit radiation which is captured by neighboring atoms and these in turn re-radiate. Thus, the radiation is trapped in the sun for a long time while it is passed from one atom to another but it eventually reaches the sun's surface and escapes. The character of the radiation changes markedly on its way to the surface. In the interior of the sun it is probably in the form of very short wavelength radiation in the X-ray region of the spectrum. As the radiation passes to the cooler outer regions, the process of absorption and re-emission gradually increases its average wavelength until, by the time the surface is reached, it is approximately in the form in which it arrives at the earth.

The surface of the sun emitting radiation is called the photosphere; it is comparatively thin, its thickness being estimated in tens of miles. When examined with a telescope the photosphere has a mottled appearance, caused by the occurrence of brilliant granules on a contrasting dark background. The granules are about 2,000 miles in diameter and have an average life of only a few minutes, indicating that they are probably caused by convection currents from hotter levels just below the surface. The edge of the photosphere is very sharply defined though its density is only about 1/10,000 that of air at sea level. It is opaque, even though it is so tenuous, because the gases of which the photosphere is composed are strongly ionized, and in this state are able to absorb and emit a continuous spectrum of radiation.

When sunspots are visible they are located in the photosphere. Sunspots appear as relatively dark regions on the surface of the sun—relatively dark because they are also at extremely high temperatures of around 4,000° C. They usually occur in groups moving from east to west across the surface indicating that the sun rotates about an axis in the same direction as the earth. The number of sunspots varies from year to year but shows a maximum about every 11 years—the well known sunspot-cycle. Much has been written about sunspots and the relations between them and phenomena on the earth. Emissions from sunspots and related phenomena have profound effects on the earth, especially the upper atmosphere, as well as affecting the electric and magnetic fields surrounding the earth. However, these emissions—astronomers and geophysicists still argue about their true nature—do not appear to penetrate in appreciable quantity to ground level, and will consequently have little bearing on a discussion concerning the utilization of solar energy.

Above the photosphere is the more or less transparent solar atmosphere which is usually seen only during a total eclipse. The region closest to the photosphere is called the reversing layer and extends for several hundred miles in height. The mean temperature in this region is appreciably lower than that of the photosphere and many of the absorption lines in the solar spectrum originate here. They are caused by atoms which absorb energy of certain wavelengths from the continuous spectrum of radiation coming from the photosphere and re-radiate it in all directions, thus weakening the original beam. In the solar spectrum these lines are only dark by comparison with the radiation of nearby wavelengths; during an eclipse, when the photosphere is hidden, they show up in the spectrum of the reversing layer as bright lines on a dark background.

Above the reversing layer is the chromosphere. This is so named because

of its scarlet color caused by the emission of a strong hydrogen line lying in the red region of the spectrum. The chromosphere is several thousand miles in height and it gradually merges into the outermost solar envelope, or corona, which appears as a filmy, pearly halo of intricate structure, stretching out hundreds of thousands of miles from the sun.

Of the 92 naturally occurring elements, over 60 are known to exist on the sun, and most of the others are probably also present but in quantities too small to be detected. Although the relative abundance of metals in the sun and the earth's crust is very similar, this is not true of the non-metals, hydrogen and helium, in particular, being much more abundant on the sun.

THE EARTH'S ATMOSPHERE

The radiation leaving the sun spreads out in all directions and 93 million miles away it may or may not hit the upper fringe of the earth's atmosphere. The radiation then has to pass through the atmosphere to reach ground level. During its passage, some of the radiation is lost because of atmospheric absorption, scattering, and other processes.

Atmospheric Absorption

The earth's atmosphere strongly absorbs radiation in the ultraviolet and infrared regions of the spectrum. Fortunately, air is practically transparent to the visible region and short distances beyond the violet and the red, and so the spectral interval containing the greater portion of the solar energy can reach ground level without being seriously depleted.

Absorption in the Ultraviolet.—The gases which absorb most of the ultraviolet energy are oxygen and ozone. Oxygen is present to heights of several hundred miles above the earth's surface and as it strongly absorbs radiation of wavelengths shorter than 1750 Å. all such solar radiation has been completely absorbed by the time it has penetrated to within 50 miles of the earth's surface. An oxygen molecule can be dissociated into two oxygen atoms when it absorbs radiation of sufficiently short wavelengths. The two resulting atoms can both receive additional energy in the form of an increase of velocity, as a result of this absorption. Consequently at great altitudes, the few atoms and molecules present are moving with great velocities which are normally associated with high temperatures.

Molecular oxygen is stable below 50 miles because no radiation is available to dissociate it; and the atmosphere is cooler because it cannot absorb much solar radiation. However, the oxygen atoms formed higher up wander to lower levels where they collide with greater numbers of other molecules as the pressure increases. Under certain conditions an oxygen atom can collide with an oxygen molecule and combine with it to form ozone. This reaction occurs most frequently at heights of 15 to 30 miles above the earth and a layer of ozone is formed in this region. Ozone strongly absorbs radiation of wavelengths shorter than 3200 Å., and thus radiation which passes through the ozone layer contains no energy below 2900 Å. because of absorption by oxygen and ozone. The energy absorbed by the ozone is sufficient to produce a marked increase in the temperature of the atmosphere just above the main ozone layer.

This atmospheric absorption is responsible for the abrupt cut-off in the energy curve, shown in figure 2, and astronomers are not certain of the shape of the solar energy curve in the far ultraviolet. One of the experiments carried out with V-2 and other rockets has been the photographing of the ultraviolet solar spectrum above the ozone layer to determine how much energy is present at wavelengths shorter than 3000 Å.

Absorption in the Infrared.—Most of the remaining solar radiation penetrates to within 10 or 20 miles of the surface of the earth with little loss. However, below

this height atmospheric pressure increases rapidly and some of the minor gases present in the atmosphere begin to absorb appreciable amounts of energy in the infrared region. These gases include water vapor, carbon dioxide, ozone, nitrous oxide, methane, and carbon monoxide. Since all of these gases have strong infrared bands, the solar energy reaching ground level is very deficient in energy of wavelengths longer than 20,000 Å.

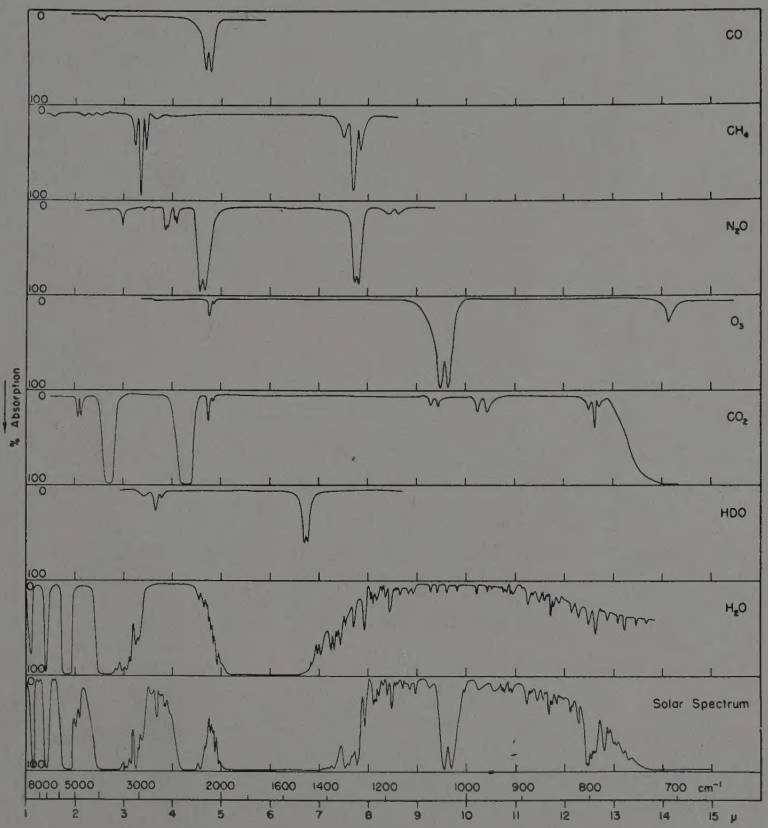


FIGURE 3. Infrared solar spectrum, from 1μ to 15μ (bottom curve), with positions and relative intensities of the bands of other known atmospheric gases shown on other curves. (1μ = 10,000 Å.)

Figure 3 shows the positions of the infrared absorption bands of the various gases. The bottom curve in this figure represents a portion of the infrared solar spectrum and shows the large energy gaps caused by these absorption bands. It can be seen that carbon dioxide and water vapor are the most important absorbers. Figure 4 shows some of the principal physical characteristics of the earth's atmosphere.

Although the atmosphere strongly absorbs in the ultraviolet and infrared, if the sun is assumed to emit radiation as a black body at 6,000° C., then 90 percent

of the radiation from the sun lies between 3,000 Å. and 20,000 Å., and most of this region penetrates to ground level without being seriously depleted.

Atmospheric Scattering

Another process reducing the amount of solar energy available at ground level is known as "scattering." The molecules and dust particles in the atmosphere pick up some of the solar radiation and then act as tiny sources of light, re-radiating the energy in all directions. Only part of this re-radiated energy is sent in the direction of the original beam. The amount of light scattered by molecules is inversely proportional to the fourth power of the wavelength. Thus, blue light, which is about half the wavelength of red light, is scattered sixteen times as much. Molecular scattering is most important at the short wavelength end of the spectrum and is the reason for the blue appearance of the sky. In addition, on hazy days, light is scattered by the dust particles and droplets present in the atmosphere in a manner nearly independent of wavelength, giving the sky a hazy, milky appearance.

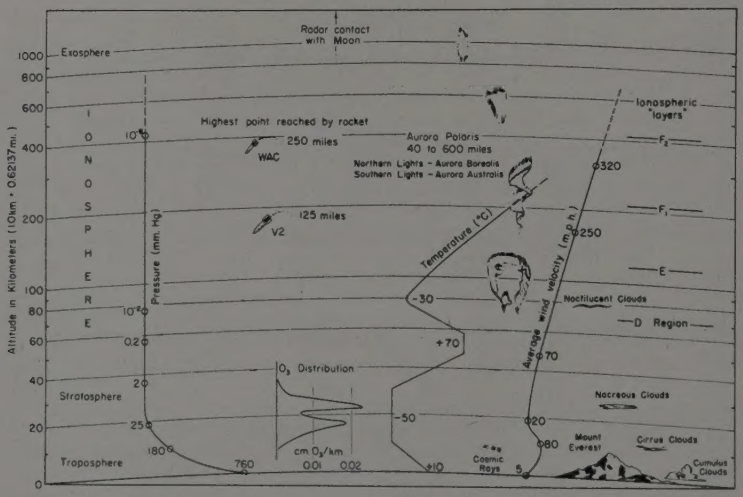


FIGURE 4. Physical characteristics of the earth's atmosphere and their variation with height; prepared from information available in 1949 by Engineering Dept., Douglas Aircraft Co., El Segundo Plant, El Segundo, Calif.

Clouds

Unless the climate is very exceptional, clouds will be present for much of the time when sunlight is available. Clouds reduce the energy reaching the ground by reflecting much of the incident energy directly into space again. The energy which penetrates thick clouds emerges from the bottom as a diffused beam because of multiple scattering by water droplets. In the process of scattering, much of the energy is also absorbed, and only a small fraction of the total incident energy reaches the ground when the sky is overcast. It should be mentioned that every thickness of cloud can occur from thin cirrostratus, which is scarcely visible and has little influence on the solar radiation, to huge banks of cumulonimbus, which absorb practically all the solar radiation.

THE AVAILABLE ENERGY OF SOLAR RADIATION

Energy is radiated from the sun at the rate of 5×10^{23} hp, so that every square yard of the sun's surface constantly emits 70,000 hp. This concentrated beam of radiation spreads out in all directions, gradually weakening with the distance from the sun and by the time it reaches the earth it is considerably reduced in intensity. The rate of arrival of solar energy, just outside the earth's atmosphere, is expressed in terms of the heat produced by the complete absorption of the radiation by a surface exposed at right angles to the beam of sunlight. The average value of this quantity (the solar constant) is about 1.94 cal./sq. cm./min. This means that energy is arriving at the rate of 1½ hp/sq. yd.—7,400 hp acre—or, the earth intercepts the equivalent in energy of burning 6 million tons of coal per second. The solar energy falling on the earth in a year is several times greater than the total energy stored in the form of oil and coal deposits.

Since all methods of using solar radiation involve the capture of energy by a surface, an acre will be taken as a convenient unit of area. An acre is 4,840 sq. yd. or roughly the size of a football field (100 yd. × 50 yd.). Although an acre exposed to the solar beam outside the earth's atmosphere receives energy at the rate of 7,400 hp, the amount reaching the earth's surface will vary with atmospheric transparency, season of the year, and time of day. With the sun vertically overhead on a clear day about 6,000 hp falls on one acre at the earth's surface.

However, the only places where the sun is ever vertically overhead lie near the equator and then the sun is in this position for a relatively short time each day. In other latitudes the amount of available energy per acre will be reduced because the sun never reaches such high altitudes. Since we are primarily interested in using solar energy in the United States, the following discussion assumes that the acre of land is situated at Columbus, Ohio, latitude 40° N., which is near the mean latitude of the United States, and the energy available per acre is calculated for this location. Other places will receive a greater or smaller amount of energy, depending on their latitude, but the difference is not large and this latitude effect will not be discussed further.

To estimate the energy which can be harvested from our acre at Columbus, the maximum energy which can be received will first be calculated and it will be shown that, for various reasons, the amount of actual available energy is greatly reduced. The figures quoted are necessarily approximate but they give the order of magnitude of the effect.

Energy Variation with Solar Altitude

When the sun is vertically overhead (90° above the horizon) energy arrives at the rate of 6,000 hp per acre; at other solar altitudes the rate at which energy arrives decreases, as shown in figure 5 and table 1. Since the solar altitude varies, it is necessary to know both the track of the sun through the sky and the length of time it is above the horizon in order to calculate the total amount of radiation falling on an acre. Both of these factors depend upon the season of the year and, consequently, the average horsepower available per acre per 24 hours varies by a factor of 4 with season, as shown in table 2. Because the losses due to atmospheric absorption and scattering depend on the path length of the radiation through the atmosphere, they will vary with solar altitude. Thus, values given in tables 1 and 2 must be further reduced to take into account these variations in energy losses and also the losses due to clouds. In addition, there are losses due to atmospheric contamination in the form of smoke and dust which vary from day to day as does the amount of cloud cover. These latter losses also vary with geographic location and, in this respect, Columbus is in a bad situation, since there are very few days when clouds are completely absent and the sky is free from haze.

For the purpose of this calculation it is assumed that the net result of all these atmospheric effects is to give an average reduction in solar energy, at all seasons of the year, of 60 percent of the values given in table 2.

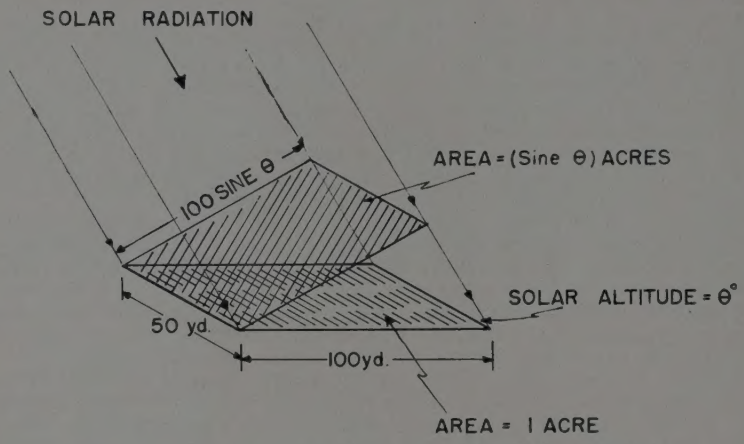


FIGURE 5. Variation in available solar radiation with solar altitude.

TABLE I
Energy variation with solar altitude

Solar altitude (Θ) above horizon	Solar energy (E) falling on 1 acre (hp) $E = E^{90°} \sin \Theta$
90°	6000
80°	5910
70°	5640
60°	5200
50°	4600
40°	3860
30°	3000
20°	2050
10°	1040
0°	0

TABLE 2
Variations in available solar energy with season

Season	Ave. solar altitude during daylight hours	Hours of available sunshine	Ave. available hp in 24 hour period
Midsummer	47°	15	2730
Spring and Autumn	32°	12	1580
Midwinter	17°	9½	700

Thus, the combined effects of the earth's rotation and the presence of the atmosphere reduce the amount of available energy per acre to the values shown in table 3, even though there is available 7,400 hp of solar energy per acre outside the earth's atmosphere.

The values given in table 3 are the ones to be used in calculating the energy crop available. To harvest this energy it must first be collected and then converted into a useful form. The methods for collecting and converting the radiation will depend on the final use of the energy. However, since any device will only convert a fraction of the incident radiation into useful energy, depending both on the theoretical efficiency of the method used and the efficiency of the actual apparatus, the final yield per acre will be much smaller than the values given in table 3.

TABLE 3

Average amount of solar energy per acre at different seasons

Season of Year	Average hp available per acre at Columbus, O., per 24 hours
Summer	1640
Spring and Fall	950
Winter	420
Yearly Average	1000

METHODS OF UTILIZING SOLAR ENERGY

There are several important factors which influence the design of apparatus for utilizing solar radiation. The most important problem is the collection of the radiation which is spread over a wide spectral interval and reaches ground level in a beam which has, for most practical purposes, a cross section of infinite area. Also, this radiation arrives in amounts which vary greatly with time.

One of the basic elements of any apparatus is a large gathering surface capable of capturing a wide spectral interval of radiation. In addition, because of the erratic nature of the radiation, the apparatus must always be ready to utilize short intervals of sunshine and should have no long "warm-up" period during which sunlight is being wasted. It must also operate efficiently when the intensity of the beam of radiation is low, as for instance, when a thin cloud bank is present, the atmosphere is very hazy or when the sun is close to the horizon. For the apparatus to be economically efficient, it must require little or no energy to keep it in working order during the time when solar energy is not available, and it should be practically automatic in operation since human attention is very expensive. Finally, for most practical uses, the apparatus must supply energy when required and not only when the sun is shining. Thus, a method of storing energy must be incorporated in the design.

These limitations impose stringent conditions on the types of methods used and also on the design of the apparatus. Other papers describe these problems in more detail and discuss ways of overcoming them. Here, the principles of the various methods proposed will be discussed and their expected efficiencies compared by making, what appear to be, reasonable assumptions. There are two main ways of using solar energy once it has been captured. These are:

(1) For space heating (e.g., houses), and

(2) For supplying energy for doing mechanical work.

The apparatus for capturing the radiation will probably be very different in these two cases.

The application of solar radiation to space heating is discussed by Professor Löf. Here, the object is to capture sufficient solar energy to be independent of other sources of heat with an apparatus as automatically efficient as a gas furnace is today, and yet at a price which is competitive with other methods of heating. Since the cost of running such a device should be negligible, the main expense will be incurred in the installation of the unit. This will depend upon the size

of the space to be heated, the complexity of the apparatus, and the amount of solar radiation available.

The efficiency and the cost of any apparatus will depend on the ingenuity of its inventor, but the quantity of radiation available depends on geographic location and season of the year. Thus, while it may be economically feasible to use solar radiation for space heating in, say, Colorado, it may be entirely out of the question in Ohio. This is discussed more fully later, but it is interesting to find that a house which uses one ton of coal a month for space heating could obtain the same amount of energy from the sunshine falling on an area of 150 sq. yd., assuming that solar energy was available at the mid-winter rate of 420 hp per acre (table 3) and that the energy converter was 100 percent efficient.

The second proposed use of solar radiation is as a source of mechanical energy. The United States contains large areas of ground of little agricultural value that receive huge quantities of solar radiation. It would seem that here is an ideal source of energy. There are several different methods of trapping this supply which all utilize the quantum nature of radiation. Sunlight was described earlier as electromagnetic radiation of different wavelengths. During the last thirty years it has been shown that there is an alternative way of describing radiation by considering it to be composed of particles or photons of different energies. With each wavelength, on the classical theory, are now associated photons with fixed amounts of energy. The energy of a photon describes its spectral position and is inversely proportional to its wavelength as measured in the classical electromagnetic theory. The intensity of the radiation is measured as the number of photons in the beam. The photons can react with matter in a number of different ways, depending on their energies, and the three main types of interaction between photons and matter, which have so far been considered for utilizing solar radiation, are described below.

Photothermal Effect.—All substances irradiated with photons absorb some of them and reflect or transmit the rest, depending upon their energies. The photons absorbed disappear, but their energy is transformed and is usually used to give the atoms or molecules composing the material, a greater degree of movement which manifests itself as an increase in temperature of the body. Here, the energy of the photon has been transformed into thermal energy and hence the heading of this paragraph. A substance which absorbs all the photons hitting it is called a "black" body and is warmed more than others which reflect or transmit some of the photons they receive. In this photothermal effect the energy of the photons is "degenerated," because it is difficult to convert thermal energy into other forms of energy although the reverse process usually occurs only too readily. All surfaces warmer than their surroundings lose heat by conductive convective, and radiative processes; and any surface irradiated with sunlight will only be heated until its rate of loss of heat is equal to the rate at which energy is received.

Heat losses occur in all heat engines, but are likely to be very large in solar heat engines unless special precautions are taken, due to the large collecting surfaces required. These considerations show that there are serious objections to methods which convert solar energy into thermal energy and then to mechanical energy; and that it is necessary to look for other more efficient methods of capturing solar radiation.

Photoelectric Effect.—Under certain circumstances the energy of a photon can be transformed directly into electrical energy. An example of this phenomenon is found in the type of camera exposure meter which has a meter to indicate the light intensity. Here, the light falls on a specially prepared surface containing atoms or atomic lattices in crystals in such a state that they can absorb photons and transfer their energy to electrons. If the photons have sufficient energy, the electrons can escape from the bonds holding them in the crystal lattice. How-

ever, photons with less than a certain minimum energy (or radiation with a wavelength longer than a critical wavelength) even though there may be many of them, will not give the electrons enough energy to escape from the lattice, and this part of the radiation must be considered wasted. By careful preparation of the sensitive surface the freed electrons can be given a preferred direction of travel so that, when light is present, the ejected electrons all travel in the same direction and produce an electric current which can then be converted into mechanical energy.

Photochemical Effect.—Another interaction between photons and matter of importance to this problem occurs when the photon energy is used to complete a chemical reaction. The best example of this is photosynthesis—probably the major natural process for converting solar radiation into useful energy. The chlorophyll in green plants captures photons and uses their energy to carry out the reaction:

$$\text{carbon dioxide} + \text{water} + \text{photon energy} \longrightarrow \text{carbohydrate} + \text{oxygen}.$$

The energy of the photon has been converted into potential energy in the carbohydrate molecule ready to reappear when the above reaction is reversed and the carbohydrate is oxidized. Although photosynthesis cannot yet be carried out in a laboratory, other types of reactions, which can be artificially controlled, are known, where photons are absorbed and their energy used to carry out chemical reactions. In these processes, as in the photoelectric process, the useful photons must have a certain minimum energy before the reaction can proceed.

These three types of interaction between photons and matter represent the basic processes available for utilizing solar energy. A number of methods based on these principles have been suggested for converting solar energy into other forms, but, as mentioned earlier, no practical solution to the problem has been found. The reason is that the types of reaction now known and the techniques available are too inefficient.

To conclude this introduction, the relative efficiencies of these three basic methods will be discussed and the energy to be expected per acre per year estimated.

EFFICIENCIES OF SOLAR RADIATION MACHINES

Any solar radiation machine must: (a) absorb as much of the available radiation as possible, and (b) convert it into mechanical energy. The overall efficiency, E, of a solar machine is the product of these two separate efficiencies and can be defined as:

$$E = \frac{\text{Useful energy obtained}}{\text{Total energy of the incident radiation}}$$

$$\left(= \frac{\text{Radiation absorbed}}{\text{Total energy of the incident radiation}}\right) \times \left(\frac{\text{useful energy obtained}}{\text{energy absorbed}}\right)$$

Efficiency of the Photothermal Process.—Surfaces can be obtained which are almost completely black so that, under certain circumstances, the fraction

$$\left(\frac{\text{Radiation absorbed}}{\text{Total incident radiation}}\right)$$

can be made almost unity. This is attempted in measuring the solar constant. However, when the radiation is used to heat the working substance in a heat engine to a high temperature, difficulties arise. As it is impractical to spread the working substance over the entire acre, some optical device is required which will collect the radiation and concentrate it on a much smaller area containing the substance to be heated. Without describing actual methods it is safe to assume that not more than one-third of the total incident radiation will be available for the next stage—conversion into mechanical energy—unless complicated and

expensive equipment is used. Losses will occur because not all the sunlight will be collected by the mirrors; some of that collected will not be concentrated on the right place; part of the energy will not be absorbed; and heat-losses are bound to occur in transferring the heated substance to the heat engine.

Further losses will occur in converting the remaining heat energy into mechanical energy. There is a physical law which enables the theoretical fraction which can be transformed to be calculated if we know the upper and lower temperatures between which the machine operates. Table 4 gives this theoretical efficiency for an engine working between various upper temperatures and a fixed lower temperature of 30° C. As the temperature difference increases, the efficiency increases, but the problems of preventing heat losses multiply rapidly and these will probably limit the upper temperatures chosen. No actual machine will operate with 100 percent of the theoretical efficiency (20 percent is usually accepted as being good).

TABLE 4

Theoretical efficiency of heat engines operating between a lower temperature of 30° C., and various upper temperatures

Upper Temp. ° C.	= Efficiency: Work produced / Energy absorbed
100	20%
200	37%
300	48%
400	55%
500	61%
1000	76%

Thus, if we had a heat engine capable of using the solar radiation falling on one acre as a source of energy and it operated between temperatures of 250° and 30° C., at 20 percent theoretical efficiency, we could only expect to have energy available at the rate of 30 hp, averaged over a year. Since no such machine has been built, this figure is, of course, only an estimate. This figure is probably optimistic and it seems unlikely that it could be improved unless very expensive, and consequently uneconomical, equipment were used.

Efficiencies of the Photoelectrical and Photochemical Processes. In these processes photons are absorbed and their energy is converted into either electrical energy or stored as chemical energy. In both cases, photons with less than some minimum energy (or radiation longer than a certain maximum wavelength) are wasted because they are unable to bring about the required reaction. Thus, in calculating the efficiencies of such processes, only a fraction of the total sunlight is of any use. This fraction

$$\left(\frac{\text{Radiation absorbed}}{\text{Total incident radiation}}\right)$$

can be determined if we know the wavelength limits of the useful radiation for a given reaction and the spectral distribution of solar energy. Table 5 shows, approximately, this theoretical efficiency—assuming that all the incident solar radiation shorter than a given maximum wavelength can be used. Considering the human eye as an energy converter, this table shows that it is sensitive to a spectral interval containing about one-half of the total solar radiation energy and is thus potentially capable of transforming this amount into other forms of energy.

However, the eye, like all other radiation converters, is not 100 percent efficient. Some energy is lost because it is not absorbed, and in all photochemical and photoelectric reactions now known, very low yields are obtained because many of the photons, which are potentially useful, dissipate their energy in the "photothermal" process and are wasted in just heating the reactants.

For a comparison with the solar heat engine, a process which absorbs 50 percent of all the solar radiation in the ultraviolet and visible portions of the spectrum and converts 10 percent of the absorbed radiation into useful energy would give 20 hp per acre on the average during a year assuming that the incident energy was arriving at the average rate of 1000 hp per acre.

TABLE 5

Table showing the theoretical efficiency of a selective solar radiation absorber which can only usefully transform radiation less than a certain maximum wavelength into energy

Critical Wavelength λ Å	Eff. = Solar energy between 3000 Å and λ crit. / Total solar radiation
3,000	0%
Violet	
4,000	4%
5,000	15%
6,000	26%
7,000	36%
Red	
8,000	47%
9,000	56%
10,000	64%
15,000	84%
20,000	90%

Thus, the energy derived would be less than that from the heat engine, and both figures show the extremely small amounts of energy which can be obtained; although 7400 hp per acre is incident outside the earth's atmosphere. Although all types of processes appear to give low efficiencies, it is easy to understand why the photochemical and photoelectrical processes look most promising for future work. As our chemical and physical knowledge increases, it should be possible to increase the practical efficiencies of these methods; whereas the efficiencies of heat engines are unlikely to be improved. In addition, heat engines will be expensive to install because of the complexity of the equipment required and maintenance costs will be high because of the attention they need. Chemical and electrical processes, on the other hand, should be practically automatic in operation and if cheap materials can be made to operate satisfactorily, no large installation costs need be incurred.

Thus, the problem of utilizing solar energy is not easy to solve, but there is reason to hope that ultimately solar energy will provide a cheap source of power as our other sources of energy disappear.

REFERENCES

The following review articles contain additional information and discussion on the subject and also give further references to earlier papers.

Ayers, E. 1950. Power from the sun. Scientific American, 183: 16–21.

Hottel, H. C. 1941. Artificial converters of solar energy. Sigma Xi Quarterly, 29: 49–60.

Report by the National Laboratory Committee (Britain). 1952. Utilization of solar energy. Research, 5: 522–531.

Trombe, F. 1947–8. Utilization of solar energy. Research, 1: 393–400.

HEATING OF AIR BY SOLAR ENERGY

GEORGE O. G. LÖF[1] AND THOMAS D. NEVENS
Denver Research Institute, University of Denver, Denver 10, Colorado

In the application of solar energy to the heating of dwellings and other uses, the primary element in the heating system is the solar collector. The function of the collector is the converting of solar radiation falling on its surface to energy in the form of sensible or latent heat in a fluid which is passed through the collecting unit.

Numerous types of solar energy collectors have been devised. The focusing type, (Muchot, 1879), employing lenses or mirrors to concentrate the solar energy onto a small, high-temperature area has been built in a variety of forms. The initial cost of this equipment appears at this time to preclude its practical use in house heating or power generation applications. Of considerably greater interest from the standpoint of economic practicability, are the several types of flat-plate solar collectors in which a fluid is heated by contact with surfaces which are heated in turn by solar radiation passing through one or more flat glass surfaces. These stationary units, vertical or sloping, have been experimentally studied in several laboratories and demonstration house installations by a number of investigators, (Hottel and Woertz, 1942; Telkes, 1950). The studies on which this paper is based have involved a solar heat collector of a stationary, sloping, flat-plate type, in which ordinary, single-strength window glass is employed both as a heat exchange surface and as an "insulating medium," which reduces escape of heat to the atmosphere.

The purpose of the collector unit employed in this development is the heating of air by passing it between overlapped glass plates and delivering the heated air to a dwelling, or to a heat-storage unit, or, in the case of air-conditioning application, to the air-conditioning unit. Associated with this purpose has been the objective of developing a permanent solar collector of minimum fixed and operating cost and pleasing appearance.

Although not the subject of this paper, several other closely related phases of the development program have been:

(1) Fundamental study of heat transfer coefficients between air and heated flat plates.
(2) Heat transfer characteristics and performance of a heat storage bed of 1-inch gravel.
(3) Performance characteristics of a solar collector of optimum design.
(4) Performance of a solar collector at temperatures suitable for air-conditioning application.
(5) Performance of a dehumidification-type air conditioner.
(6) Design and predicted heating costs for solar heated houses in Denver, Colorado and Dallas, Texas.

This paper deals with the studies associated with the performance of the most efficient form of the solar collector under winter heating conditions. Primary objectives have been the determination of the relationships between useful heat recovery, solar intensity, outdoor ambient air temperatures, type and arrangement of glass plates in the unit.

[1]Present address: Consulting engineer, 1608 Broadway, Denver, Colo.

THE OHIO JOURNAL OF SCIENCE 53(5): 272, September, 1953.

DESCRIPTION OF APPARATUS

In order that the function and arrangement of the collector may be more clearly evident, the general arrangement of the complete solar heating system in a dwelling may be outlined. The collector unit of suitable area is located in the roof of the dwelling, flush with the roofing surface; air circulated up the sloping collector between its glass surfaces, enters a manifold at the collector exit, passes to a fan, and then either to the rooms of the dwelling or into the top of a vertical storage bin of 1-inch to 1½-inch gravel. If the air is being directed to the rooms of the house by the thermostatic controls, it finally leaves them via the cold air return and passes through ducts to the collector inlet. If, however, heat is being stored, the air after delivering its sensible heat to the gravel bed, leaves the bottom of the bin and returns through a duct to the collector inlet. Finally, when the house requires heat at night, air is drawn from the rooms through the cold air return duct to the bottom of the storage bin, is heated by its passage through the gravel, and is forced by the blower through the heating duct to the rooms. An auxiliary duct heater is incorporated in the system for use when solar heat is not available.

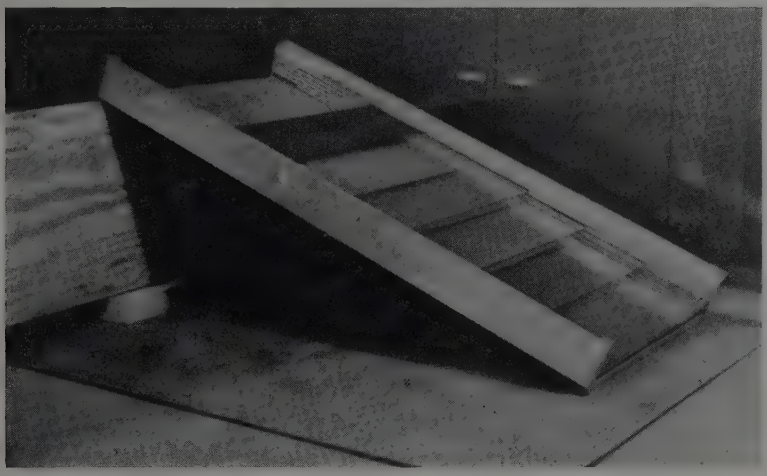


FIGURE 1. A solar collector.

The solar collector, as presently developed, consists of a multiple of individual units 2 ft. × 4 ft. in size. A series of four such units, each comprising a thin sheet-metal trough approximately four inches deep and an arrangement of glass plates, is shown in figure 1.

The basic heat-recovery element in the unit consists of a pane of single strength window glass 2 ft. × 18 in. coated with a black heat absorbing surface the entire two feet width of the plate for a distance of six inches along the 18-inch length. A number of these plates supported at their edges by one of several arrangements is installed in the unit, black surfaces uppermost, and overlapped so that each black surface is beneath two clear surfaces. In the presently-employed construction, spaces of one-fourth inch are provided between successive plates. At the two ends of the unit, 6-inch and 12-inch plates are installed so that a uniform exposure of black plates is obtained. Above the entire series of overlapped plates, and resting on the top edges of the trough, a single sheet of glass 2 ft. × 4 ft. in size is supported. In some trials, two and three such cover plates were employed.

The heat absorbing surface presently employed is a dull surface of black glass fused to the surface of the pane.

The basic principle of the overlapping plate arrangement with the theory of of its function was first described by Miller (1943), and is similar to the "greenhouse effect". This effect depends upon the fact that glass is transparent to visible and short infrared wavelengths which make up the predominate portion of sunlight and is opaque to long infrared wavelengths such as originate in black bodies below 500° F. When the sunlight enters a glass-covered enclosure, it impinges on the contents, is absorbed, thereby heating the interior surfaces which then emit low temperature, long wavelength radiation which is trapped inside the glass enclosure. Thus, when the collector is exposed to solar radiation, the black surface will become heated to an elevated temperature which may be in the vicinity of 300° F. This surface will radiate to the clear surface above and heat it to some lower temperature, such as 200° F. This surface will in turn heat the one above it to still a lower temperature— say 100° F. and finally that surface will heat the cover plate to a temperature a few degrees above the surrounding atmosphere. Because of symmetry

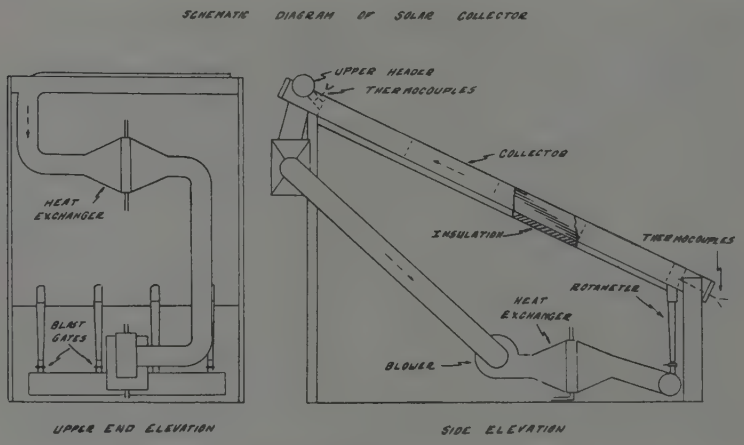


FIGURE 2. Schematic diagram of a solar collector.

in the unit, this vertical temperature gradient is duplicated along a single plate; thus, the air passing between two adjacent plates encounters a progressively rising temperature until it leaves the end of the black surface at the maximum temperature.

The low air velocity employed (about 1 ft./sec.) introduces very little turbulence between plates, thereby causing little convection loss from plate to plate. Hence, the principle factors contributing to the loss of heat from the unit are the plate-to-plate radiant transfer described above, and essentially pure heat conduction through the streamline air layers and glass plates. By the arrangement of black and clear glass areas, it is therefore possible to heat air to a temperature closely approaching that of the black surface.

The complete experimental collector employed for the studies of performance is diagrammed in figure 2. The collector, mounted on a 27° south slope, consists of sixteen individual 2 ft.×4 ft. troughs. These are arranged in four rows of four units each. Two finned-tube heat exchangers are provided in the air circuit for air

temperature control. A blower of the flat-blade centrifugal type is used for air circulation.

The individual collector units are supported at their top edges and sides by wooden rafters. Glass-wool insulation is provided beneath the collector troughs and on all air ducts.

In most of the tests, each of the four rows was provided with a different cover plate arrangement. In two of the troughs, ordinary single strength glass was used, one was provided with single cover plates, the other with double cover plates separated by a ¼-inch air space. In the other two troughs, surface-treated glass was used throughout; single covers were used on one, double on the other. The treatment of the glass involved the formation of a surface film of silica, one-fourth wavelength in thickness. This etching process, developed by RCA (Nicall, 1942) for reducing surface reflection, was found to be highly satisfactory.

Instrumentation consisted of four rotameters, one in each of the four rows; thermocouples were installed at the inlet in each row and at the exit connector duct leading from the upper end of each trough into the hot manifold. Gate valves were provided at the rotameter inlet for control of the air circulation rate.

Apparatus other than that employed in the collector system itself consisted of an Eppley ten-junction pyrheliometer for measurement of solar energy input at a 27° angle, a Leeds and Northrup Recorder for this instrument, and a 12-point recorder for temperatures throughout the unit.

EXPERIMENTAL PROCEDURE

The studies performed with the present collector arrangements may be divided into two phases, those involving winter operation with house heating application, and those in which air was recirculated through the unit at moderate or high temperatures in order that performance under conditions required for air conditioning could be obtained. Although similar operating procedures were employed in these two types of tests, the detailed steps differed to some degree; techniques employed in the heating study are specifically described here.

The general procedure consisted of operating the collector on cloudy as well as sunny days in order that measured heat recoveries would be representative of those which would be obtained during a normal operating season. During a day's run of the collector, measurements of the air temperatures at the inlets and outlets of all four rows were continuously recorded. The air flow rate was held constant and identical in each of the four rows, as indicated by the rotameters. Solar intensities on the phyrheliometer, positioned at an angle of 27° facing south, were continuously recorded.

Operation of the collector during any one run consisted of starting the circulating blower in the morning as soon as the temperature of the air leaving the collector could be as high as approximately 80° F. The gate valves at the inlet to each row were then adjusted to a predetermined air rate. As soon as the entrance air temperature rose to 65° F, cooling water was run through the two heat exchangers and the water rate adjusted so that the air entering the collector would remain at 65° F. (the temperature at which air would ordinarily be recirculated from a home to the collector in winter operation).

By dependent variation of air flow rate and inlet air temperature, the experimental results could be employed in correlations of heat recovery and exit air temperatures as affected by solar input rate, air rate, cover plate arrangement, inlet air temperature, ambient air temperature, time of day, and reflectivity of glass. Experimental data were obtained at air flow rates of 0.40, 0.76, 1.12, 1.43, and 1.82 standard CFM per square foot of collector area. Mean daily ambient air temperatures varied from 0° to 65° F while the total daily solar radiation varied from 400 to 2,800 BTU/sq. ft. of collector area.

DISCUSSION OF RESULTS

In figure 3, typical results of performance in a single day's operation of two rows of the collector are shown. Outlet and inlet air temperatures, heat recovery, and solar radiation are plotted against time of day. These data were secured on April 16, 1951, a clear day, at a mean ambient air temperature of 44° F and an air rate of 1.12 standard cu. ft. (measured at 760 mm pressure and 70° F) /min./sq. ft. of collector area. The average inlet air temperature was maintained at approximately 65° F. The useful heat recovered was considered as the heat recovered above 70° F whenever the outlet air temperature from the collector was at least 80° F, the minimum temperature at which heat could in all probability be economically recovered. Barometric pressure in the collector was approximately 630 mm.

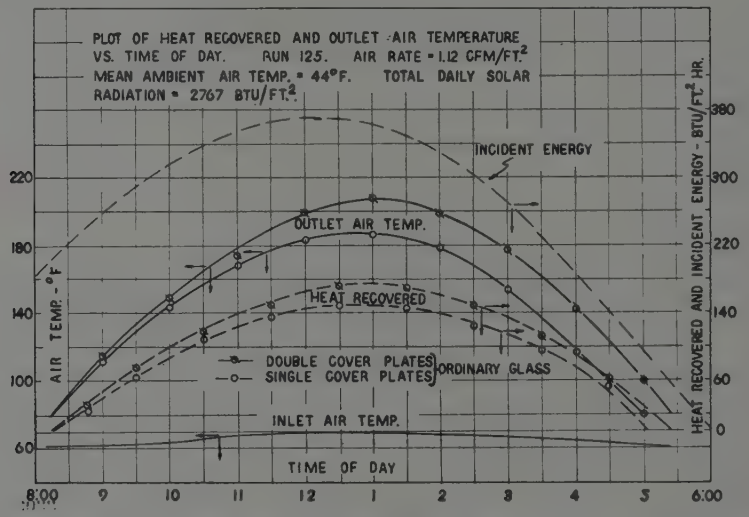


FIGURE 3. Plot of heat recovered and outlet air temperature vs. time of day. Run 125. Air rate = 1.12 cfm/ft². Mean Ambient air temp. 44° F. Total daily solar radiation = 2767 BTU/ft.²

It is seen from the curves that the exit temperature and heat recovery both increase from comparatively low values in the early morning to maximum values at approximately 1:00 P.M. and then decrease to low levels in the late afternoon. The temperature and heat recovery curves do not reach a maximum at noon as does the solar radiation because of sensible heat storage in the glass and other components of the collector. The rather wide variation of temperature and heat recovery are of course due to the change in solar intensity throughout the day; if desired, the temperature variation could be reduced by adjusting the air rate from time to rime rather than holding it constant. Heat recovery efficiency may be visualized by noting that the area under each heat recovery curve divided by the total area under the solar radiation curve is equal to the efficiency.

In figure 4 are shown the performance characteristics of a row provided with ordinary glass and single cover plates when operated at an air flow rate of 1.12 CFM /sq. ft. of collector area. Useful heat recovered is plotted against total daily incident radiation, with ambient air temperature as parameter. Each point

on the plot represents a single day's run; ambient air temperature was the Weather Bureau mean for the 24-hour period beginning at 12:00 mid-night. The lines through the data points indicate that heat recovery rises nearly linearly with an increase in incident solar radiation. It can easily be shown that the efficiency, i.e., heat recovered divided by the total incident energy, is not constant, but varies both with total daily incident energy and ambient air temperature.

From theoretical consideration, it is evident that the mean ambient air temperature is a suitable parameter in the correlation of heat recovery. Since the solar collector is exposed to the atmosphere, during the night the temparature of the materials in the collector will approach the ambient air temparature, or on clear nights may drop below air temparature because of radiation to the sky; on a day following a cold night considerable solar radiation will be required to heat the

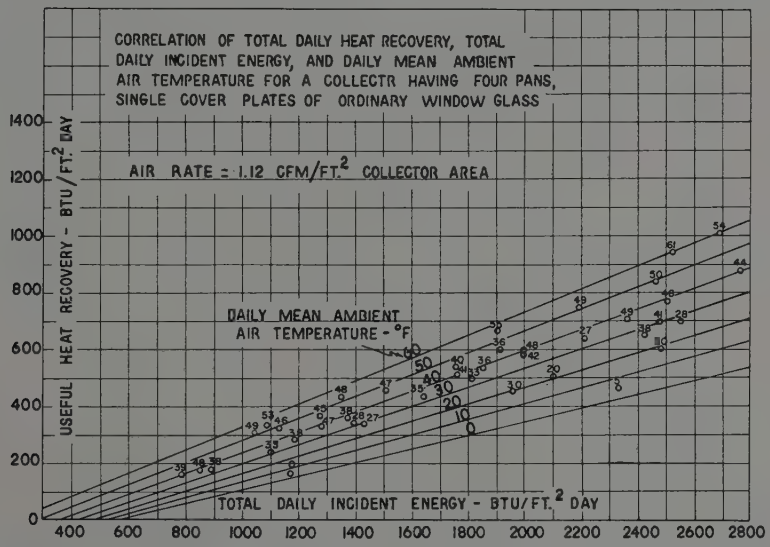


FIGURE 4. Correlation of total daily heat recovery, total daily incident energy, and daily mean ambient air temperature for a collector having four pans, single cover plates of ordinary window glass.

glass in the collector to a temperature at which useful heat may be recovered. Also, on a day of low ambient air temperature, the radiation and conduction loss from the collector during daylight operation will be larger than during warm weather. Conversely, on a warm day following a warm night, the sensible heat lag of the collector and the radiation and conduction losses will be smaller so that more useful heat may be collected per unit quantity of solar radiation. As can be seen in figure 4, the radiation and conduction losses during the day and the sensible heat lag resulting from the previous night's ambient air temperature are such that for a particular total daily solar radiation and air rate, the useful heat recovered rises nearly linearly with mean ambient air temperature.

As seen in figure 4, the experimental points generally show deviations from the mean within approximately 5 percent. In all cases of larger inconsistency, the deviations may be attributed to any one or several of the following factors;

(1) The mean ambient air temperatures (the mean of the high and low temperatures for a 24-hour period beginning at 12:00 mid-night) as given by Weather

Bureau records do not represent the mean temperature during the day and previous night. An example might be a 24-hour period in which the ambient air temperature was high for the day and the previous night, but was abnormally low during the early evening following the day's collector operation.

(2) A low overcast sky in which case the radiation loss from the collector cover plates will be lower than during a clear day.

(3) Abnormally high winds causing large conduction losses. However, even with these variations, the data show a maximum deviation of approximately 10 percent.

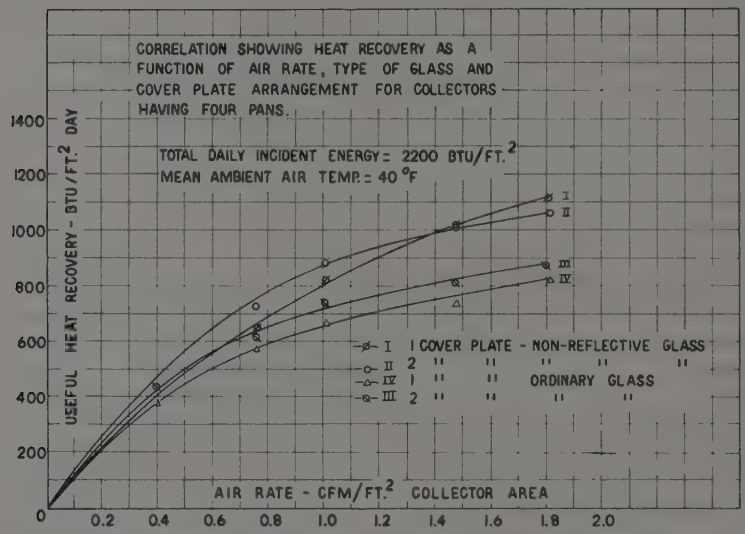


FIGURE 5. Correlation showing heat recovery as a function of air rate, type of glass and cover plate arrangement for collectors having four pans.

The relationship between useful heat recovery, air flow rate, cover plate arrangement, and ordinary and non-reflective glass for a total daily solar radiation of 2,200 BTU sq. ft. and a mean ambient air temperature of 40° F. is shown in figure 5. It is seen that useful heat recovery rises as air circulation rate is increased and that there is a considerable difference in the performance of collector rows having different cover plate arrangement and ordinary or non-reflective glass. The fact that heat recovery increases with air circulation rate, results from the lower exit air temperatures and glass temperatures and corresponding reduction in heat loss from the cooler collector unit. As seen in figure 5, the heat recovery at a given air rate is considerably greater for collectors provided with non-reflective glass than collectors having ordinary glass. This difference may be attributed to the higher transmittance of the non-reflective glass.

It is noted that the heat recovery for a row having single cover plates and non-reflective glass (Curve I) is higher than the heat recovery for a row having double covers and non-reflective glass (Curve II) at air rates greater than 1.5 CFM sq. ft. of collector and that at air rates below this value the recoveries are reversed. This may be explained by consideration of the relative magnitude of

the radiation and the reflection losses from the collector. At low air rates, at which high cover plate temperatures prevail, the reflection loss for double covers is small relative to large radiation losses from single cover plates. At high air rates and correspondingly lower cover plate temperatures, the reverse is true.

It is observed that the heat recovery for a row having single cover plates and ordinary glass (Curve IV) is lower than the heat recovery for a row having double covers and ordinary glass (Curve III) over the entire range of air rates shown. Again, this may be explained by consideration of the relative magnitude of the radiation and reflection losses from the collector. In contrast to the relatively low reflection losses of non-reflective glass, the ordinary glass exhibits relatively high losses compared to the radiation and conduction losses over the range of air rates shown.

Although final choice of cover plate arrangement and type of glass used in the collector will depend upon the result of an economic balance, it is thought that the probable desirable type of arrangement will be with the use of single cover plates and non-reflective glass. With this cover plate arrangement, and at an air rate of 1.5 CFM/sq. ft. of collector area, which is in the approximate range of operation that would probably be used for commercial operation, heat recovery on a clear day at a mean ambient air temperature of 40° F would be about 50 percent of the total daily incident energy.

It is estimated that the maximum error in determination of the total daily incident energy is ± 2 percent. Calibration of the thermocouples used for all temperature measurements indicated a maximum error of ± 2° F. The four Flowrators used for air flow measurements were calibrated with a positive displacement gas meter which indicated a maximum percentage error of 4 percent at the lowest air rates employed. It is estimated that the heat recoveries deviate not more than 5 percent from their true values.

CONCLUSIONS

Studies of the performance of a solar energy collector of the overlapped glass plate type have resulted in the following conclusions:

(1) A solar energy collector unit has been developed which should be produceable on a factory basis, and suitable for installation in a new dwelling without extensive fabrication at the site.

(2) At a particular air rate and total daily solar radiation, the useful heat recovered increases approximately linearly with the mean ambient air temperature.

(3) At a particular air rate and mean ambient air temperature, heat recovery increases linearly with an increase in total daily solar radiation.

(4) At a particular total daily solar radiation and mean ambient air temperature, the heat recovery increases with air rate.

(5) The heat recovery for a row provided with single cover plates and non-reflective glass is higher than the heat recovery for a row provided with double covers and non-reflective glass at air rates greater than 1.5 CFM/sq. ft. of collector; at air rates below the value the recoveries are reversed.

(6) The heat recovery for a row having double cover plates of ordinary glass is greater than a row having single cover plates over the range of air rates studied.

(7) The heat recovery of a row having non-reflective glass is appreciably greater than a row having ordinary glass.

(8) With a collector as designed, heated air ranging in average temperature from 120° to 180° F. at heat recovery efficiencies in the vicinity of 50 percent can be delivered to a dwelling on sunny winter days at 40° latitude.

ACKNOWLEDGEMENTS

The authors wish most gratefully to acknowledge the generous support to this solar energy program by the American Window Glass Co. of Pittsburgh, Pennsylvania, and to Mr. A. S. Crandon, Mr. H. W. McIntosh and Dr. F. L. Bishop, Jr., of the Company, who have been most helpful with suggestions and encouragement. Their permission to publish the results of these studies is also gratefully acknowledged. The contribution of Mr. F. A. Hasenkamp who helped procure and compile most of the data in this paper is acknowledged.

REFERENCES

Hottel, H. C., and **B. B. Woertz.** 1942. The performance of flat-plate solar heat collectors. Trans. A.S.M.E. 64: 91–104.

Miller, K. W. 1943. Solar heat trap. Unpublished memorandum to the Office of Production Research and Development, War Production Board (July 12).

Mouchot, A. 1879. Solar Heat, Its Industrial Applications. Ganthier-Villars, Paris.

Nicall, F. H. 1942. A new chemical method of reducing the reflection of glass. RCA Review 6: 287–301.

Telkes, M. 1950. Low-cost solar heated house. Heating and Ventilating, 47: (Aug.) 72–74.

PHOTOSYNTHESIS

PAUL ROTHEMUND

The Charles F. Kettering Foundation, Yellow Springs, Ohio

During the activities of growth, maintenance, and repair, the living organism converts food materials into protoplasmic and structural constituents, or into energy. This assimilatory process applies to plants and animals alike, and it is accompanied by the process of respiration, that is, atmospheric oxygen is taken into the cells, the various organic substances are partially or completely oxidized, and carbon dioxide is produced and eliminated.

The green plant is capable of performing the reduction of carbon dioxide (the most depreciated form of carbon in nature) under liberation of free oxygen, and it can do so only in light. The carbon, which became available in the reaction, is used to synthesize the numerous constituents of the plant and the process is called "assimilation of carbon" or "photosynthesis." The reduction of carbon dioxide, as such, is not exclusive with green plants; besides normal photosynthesis, one has observed that certain purple bacteria and unicellular algae can reduce carbon dioxide in light with the simultaneous consumption of inorganic or organic hydrogen donors (Gaffron, 1933, 1944; Van Niel, 1931). In the dark, the reduction of carbon dioxide is often accompanying enzymatic processes, such as the metabolic reactions in animal tissues, or bacterial fermentation by methane and by propionic acid bacteria, oxidations in plants and unicellular algae, and bacterial oxidations, as in the sulfur bacteria (Krebs, 1943; Werkman and Wood, 1942). The three different types of biological reduction of carbon dioxide may be demonstrated with unicellular algae of the family *Scenedesmus*. Gaffron (1944) was able to have these organisms perform at will the chemo-reduction of carbon dioxide in the dark by burning hydrogen with oxygen to water — a photoreduction in which 2 molecules of hydrogen and one molecule of carbon dioxide disappear — and the normal photosynthesis, in which, for each reduced molecule of carbon dioxide, the equivalent amount of oxygen is liberated.

For the purpose of further discussion here, photosynthesis by green plants will be considered mainly. In light it is superimposed upon the respiration process; the two processes may be represented schematically as follows, when a hexose sugar is used for the purpose of illustration:

$$6\ CO_2 + 6\ H_2O + 672\ \text{kcal.} \xleftarrow[\text{Respiration}]{\text{Photosynthesis}} C_6H_{12}O_6 + 6\ O_2$$

Photosynthesis is, of course, not limited to carbohydrate production. Its several steps involve enzymatic reactions; and one may define it as an enzymatically controlled oxidation-reduction, brought about by radiations from the visible region of the solar spectrum, and causing the reduction of carbon dioxide under simultaneous oxidation of water, or of another hydrogen donor.

THE ASSIMILATORY SYSTEM

The green parts of plants differ widely in structure throughout the plant kingdom. In most plants the cells contain the green pigments in the chloroplasts,

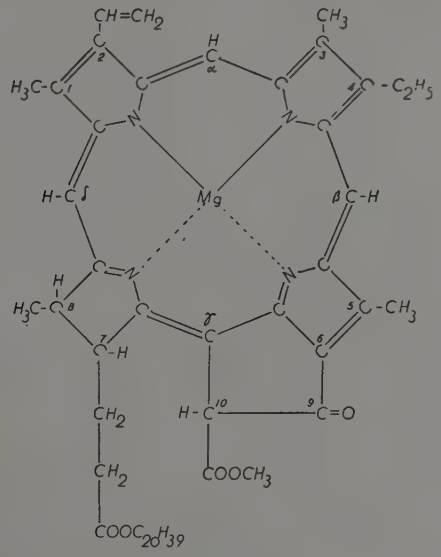


FIGURE 1. Chlorophyll *a*.

which are usually spherical or double convex protein-containing bodies. The cells of most plants contain a large number of chloroplasts, but in some of the algae only one single large chloroplast is found in each cell; in others the pigments are not localized, and are fairly evenly distributed throughout the cells.

The coloring matter in the chloroplasts of green plants is a mixture of pigments. By suitable extraction and separation methods one obtains usually two green pigments (chlorophyll *a* and chlorophyll *b*), a number of yellow and orange substances belonging to the carotinoids, and from some plants red and blue pigments, phycoerythrin and phycocyanin, respectively. In certain bacteria a special bacteriochlorophyll has been found (Fischer and Hasenkamp, 1935). All living cells also contain specific pigments, the cytochromes, which are important in biological oxidations.

The individual pigments are chemically identical, irrespective of the plant from which they were isolated, but their relative amounts vary greatly. In many higher plants, the ratio of the blue-green chlorophyll *a* to the yellow-green chlorophyll *b* is about 3 : 1. In some plants the ratio is greatly different and in certain green algae, as well as in the classes *Rhodophyceae*, *Pheophyceae*, and *Cyanophyceae*, and in the family *Diatoms*, only chlorophyll *a* is found, but no chlorophyll *b* (Seybold, Egle, and Hülsbruch, 1941). In the groups of purple and brown bacteria several derivatives of chlorophyll occur (Van Niel and Arnold, 1938). The green pigments (chlorophyll *a* and *b*) are the most important ones for the process of photosynthesis. They are complicated pyrrole pigments, and contain magnesium in complex linkage in the molecule. Figures 1 and 2 indicate the present

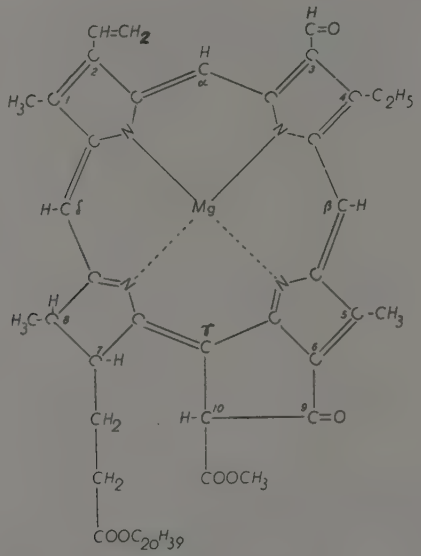


FIGURE 2. Chlorophyll *b*.

concept of the chemical structure of these two pigments, and the numbering system according to Hans Fischer. The two chlorophylls differ only with respect to the substituent in position 3 of the molecule; in chlorophyll *a*, a methyl group (CH_3) is found, in chlorophyll *b*, the aldehyde group $\left(\begin{matrix} C \\ \diagdown \\ \diagup \\ O \end{matrix}\!\!\begin{matrix} H \\ \\ \\ \end{matrix}\right)$. This difference has caused much speculation, whether the two pigments could be partners in an oxidation-reduction system, but the absence of chlorophyll *b* in so many plants, and the complete lack of direct experimental evidence have eliminated this view. The structure of bacteriochlorophyll is closely related to that of the other two green pigments, as figure 3 indicates. The formulae of these pigments have not been confirmed by synthesis as yet, however their chemical properties are treated in detail in H. Fischer's book on pyrrole chemistry (Fischer and Orth, 1943). A review on chlorophyll may be found in Medical Physics (Rothemund,

1944); its technical production and uses are the subject of a recent summary (Rothemund, 1949).

MEASUREMENT OF PHOTOSYNTHESIS

A great number of methods for the determination of the yield, or of the rate of photosynthesis under natural and controlled conditions have been devised. They may be classified according to the kind of determination performed: (a) absorption of carbon dioxide, (b) evolution of oxygen, (c) production of carbohydrate, (d) determination of the fluorescence intensity of the pigments, and (e) use of stable (e.g., ^{2}H, ^{13}C, ^{18}O) or of radioactive isotopes (e.g., ^{3}H, ^{11}C, ^{14}C). To all these methods one difficulty is common, namely, the influence of plant respiration on the result. For detailed descriptions of the different methods of

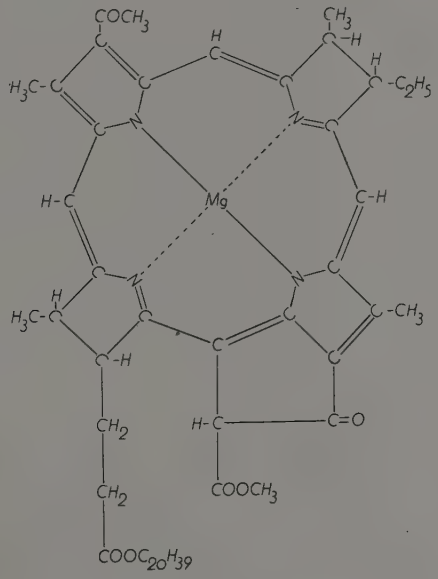


FIGURE 3. Bacteriochlorophyll a.

measurement and for their critical evaluation, the reader is referred to several monographs on photosynthesis (Spoehr, 1926; Rabinowitch, 1945, 1951; Franck and Loomis, 1949).

Some authors claim that the continuous analysis by mass spectrography of gases containing oxygen isotopes may be used to establish the effect of light on the respiratory rate of plants. No increase of respiration in light as compared with the respiration in the dark has been reported so far, but photoinhibition of respiration up to 100 percent seems to occur in certain organisms [Personal communication, reported by Gaffron and Fager (1951)]. It must be kept in mind, however, that all experiments with isotopes in biological systems may suffer from secondary reactions, namely, the exchange of isotopes, and the possible discrimination for or against one or more isotopes. Thus, it has been reported that in the measuring of photosynthesis in *Chlorella* and barley, at about 1,000 foot candles the ratio of utilization of isotopes was:

$$^{13}C/^{12}C = 0.96,\ ^{14}C/^{12}C = 0.85, \text{ and } ^{14}C/^{13}C = 0.89$$

(Gaffron and Fager, 1951), showing discrimination against the heavier isotope in each case. (The discrimination against ^{14}C was considered especially noteworthy.)

In order to determine the rate of photosynthesis, reliable measurements of the total incident light and of the radiation actually transformed into chemical energy in the plant must be obtained. The total energy received by the tissue is not entirely utilized for photosynthesis, but also in such other processes as transpiration, transmission, reflection, thermal emission, and fluorescence. Experimental difficulties in measuring the share of such losses of radiation exactly are responsible for much contradiction in the literature concerning the utilization of energy in photosynthesis.

FACTORS INFLUENCING PHOTOSYNTHESIS

The photosynthetic apparatus of the green plant is influenced in its operation by a number of factors, which may be conveniently classified as internal and external. The proper interaction of these factors leads for each organism to an optimum value for photosynthesis; variations in the relative share of each factor in the process may cause photosynthesis to cease entirely, or, on the other hand, reach a maximum of performance. The important internal factors are:

(1) anatomical structure of the tissue
(2) chlorophyll content of the cells
(3) enzyme system in the protoplasm and in the chloroplasts
(4) influence of reaction products of photosynthesis and their accumulation on the progress of the reaction
(5) freedom from pathological conditions.

External factors may be listed as follows:

(1) concentration of carbon dioxide
(2) concentration of oxygen
(3) intensity and frequency of incident light
(4) temperature
(5) water supply
(6) supply of nutrient salts and trace elements
(7) substances not encountered normally by the plant (irrespirable gases, anaesthetics, toxic materials, etc.)
(8) effect of hydrostatic and of osmotic pressure in aquatic plants
(9) influence of mechanical injuries
(10) electrical conditions (atmospheric or applied intentionally).

No detailed discussion of each of these factors can be given here, but a few observations should be mentioned. Experiments with cell triturates show that the photosynthetic apparatus operates even though the entire structure of the cell has been destroyed so that microscopic examination reveals absence of intact cells.

Variations in the rate of photosynthesis may also occur under physiological conditions without the activity of a limiting factor simply by processes like "resting," or by phenomena like "aging" of the plant.

Many investigators perform photosynthesis experiments on cells or parts of plants, which are working under much higher concentrations of carbon dioxide than that normally encountered by the plant under study. For low carbon dioxide concentrations, there is approximate proportionality between rate of photosynthesis and concentration. For higher concentrations, the observers disagree -some find indirect proportionality; others report direct proportionality up to a certain point, and they assume that from then on some other factor becomes limiting. Such a factor may be the temperature. It has been shown that the rate of photosynthesis under excess carbon dioxide is strongly influenced by temperature. Continuation of the experiment with very high concentrations causes a decrease of the photosynthetic rate, most likely due to the unphysiological conditions used.

The relationship between photosynthesis and light intensity depends greatly upon the plant under investigation (shade plants and sun plants differ in their response to changes in light intensities). In general, the behavior of plants to variations of light intensity is similar to that under variations of carbon dioxide concentration—proportionality up to a certain point, leveling off smoothly or sharply at the "saturation level," where probably another factor becomes limiting, and finally a decrease. The latter is interpreted as either mechanical response of the plant to high light intensities (or carbon dioxide concentrations), or as a consequence of the poisoning of the photosynthetic system. Some plants do not form starch continuously when exposed to light, but either stop after a certain length of time or even redissolve the starch already formed. Ursprung (1917) called this phenomenon "solarization"; it is not accompanied by permanent injury of the plant's photosynthetic abilities.

While respiration is believed to be, for most plants, independent of light intensity, if experiments are performed of sufficiently short duration, the rate of photosynthesis increases up to a certain point. There exists then a light intensity at which the net gas exchange becomes zero, when the two processes—respiration and photosynthesis—furnish and use, respectively, identical volumes of carbon dioxide or oxygen. This light intensity is called the "light compensation point." For some unknown reason, there exists a great variation in the value of the compensation point for different species of plants. It is lower in shade plants than in sun plants, and it does not seem to be a function of the respiratory activity of the plant.

For intermittent irradiation and high light intensities, the rate of photosynthesis is larger than for continuous illumination, referring to equal total time elapsed during the light periods. Under low light intensities, intermittent illumination does not exhibit such an influence on photosynthesis (Warburg, 1919). After a period of darkness, the cell, again exposed to light, does not operate immediately at the same intensity level at which it had ended its work during the preceding period of illumination. This phenomenon is called "photochemical induction." Usually light and dark periods follow each other in rapid succession. Different plants vary in their responses to the same frequency of light and dark changes. By suitable choice of plant material and frequency of light and dark periods, the influence of photochemical induction may be brought to a minimum. The fluorescence of the chlorophylls under intermittent light also rises to its full value only gradually after a dark period.

Various chemical substances are used in order to influence selectively certain defined steps in the photosynthetic process. By using the proper inhibitor for a particular reaction, or a process like respiration, or an enzyme system, other unaffected sequences in photosynthesis may be studied independently. Many inhibitors are very specific; e.g., narcotics and cyanide. Through skillful selection of substances and experimental conditions many of the important results in our present knowledge of photosynthesis were established. Since many conclusions drawn from biological material are holding only for one family, or one species, selected algae or bacteria, grown in pure culture, are used. These organisms often adapt themselves to variations in living conditions, and may sometimes even be "trained" to accept conditions which were formerly unphysiological for them.

PRODUCTS OF PHOTOSYNTHESIS

The outstanding gaseous product of photosynthesis is oxygen. The ratio:

$$Q_P = \frac{\text{Moles } O_2 \text{ liberated}}{\text{Moles } CO_2 \text{ absorbed}}$$

is called the photosynthetic quotient, or assimilatory quotient. Its numerical

value is, with relatively few exceptions, unity or surprisingly close to it. The respiratory quotient is the inverse ratio of the above: or

$$Q_R = \frac{CO_2}{O_2}$$

According to the schematic equation for photosynthesis, given on page 281, carbon dioxide is reduced, and a simple sugar is obtained under evolution of oxygen. For a long time it had been assumed that the reduction led to formaldehyde, which then condensed to the sugar. Polymerization of the latter causes the formation of starch in the leaf. Leaf starch was demonstrated as early as 1862 by J. Sachs. The formaldehyde hypothesis was suggested in 1870 by A. von Baeyer, who based it on a previous observation by A. Butlerow (1861). It was tested in experiments with isotopic carbon with the result that formaldehyde is now considered very unlikely as an intermediate in photosynthesis (Ruben, Hassid, and Kamen, 1939; Ruben, Kamen, and Hassid, 1940; Ruben, Kamen, and Perry, 1940). And the use of oxygen isotope ^{18}O proved that all the oxygen evolved comes from water molecules, and not from the carbon dioxide (Ruben, Randall, Kamen, and Hyde, 1941; Dole and Jenks, 1944). Photosynthesis is actually making use of hydrogen from the water to reduce carbon dioxide, and the hydrogen is obtained by photolytic fission of the water molecule—it is not a hydration of carbon, as the term carbohydrate might indicate. The equation may be simplified by referring only to one molecule of carbon dioxide, and indicating the oxygen isotope by an asterisk, as follows:

$$CO_2 + 2\ H_2O^* + 672\ \text{kcal.} \longrightarrow [\![CH_2O]\!] + H_2O + O_2^*$$

$[\![CH_2O]\!]$ no longer represents a formaldehyde molecule but symbolizes here that simple structural unit, which through condensation and polymerization reactions, will ultimately build up the starch molecule in the plant.

This view of the process is supported by photosynthesis experiments with purple bacteria (Van Niel, 1941; Franck and Gaffron, 1941), in which hydrogen sulfide furnishes the hydrogen for the reduction of carbon dioxide under elimination of sulfur, according to the equation:

$$CO_2 + 2\ H_2S + \text{energy} \longrightarrow [\![CH_2O]\!] + H_2O + D_2,$$

and by experiments with specially conditioned algae, which are able to use gaseous hydrogen directly. In the latter case, no evolution of oxygen takes place, as shown in the scheme:

$$CO_2 + 2\ H_2 + \text{energy} \longrightarrow [\![CH_2O]\!] + H_2O.$$

In the search for analogies *in vitro* for the formation of gaseous oxygen in light, with the help of chlorophyll or chlorophyllous materials, several working combinations have been reported. When water and carbon dioxide are exposed to light in the presence of chlorophyll, geraniol, glycerol, and methylene blue molecular oxygen and formaldehyde are formed; the production of percarbonic acid as reaction intermediate has been suggested (Baur, Gloor, and Künzler, 1938; Baur and Niggli, 1943). The so-called "Hill reaction" is a chlorophyll-sensitized reduction of ferric to ferrous iron under oxygen evolution according to the equation:

$$4\ Fe^{+++} + 2\ H_2O \xrightarrow{\text{light}} 4\ Fe^{++} + 4\ H^+ + O_2,$$

and can be brought about with chloroplast suspensions or leaf meal (Hill, 1937, 1939). Oxygen evolution also takes place by the action of light on quinone (Warburg and Lüttgens, 1944).

Starch, the other readily demonstrable product of photosynthesis, has been studied for a long time; but only during the past decade the fact was recognized that natural starch is a heterogeneous material. The two main components of ordinary starches are amylose, made up of long unbranched chains of glucose

residues, and amylopectin, consisting of highly branched short chains. (Schoch refers to the two components as fraction A, and fraction B, respectively.)

There is general agreement that starch formation in the plant is not part of the photosynthetic process proper, but rather the result of a secondary reaction. This view is supported by the fact that the leaves of many plants are starch-free, and that most plants are able to convert sugars into starch in the absence of light. The numerous biological transformations of starch are reviewed in a recent article (Peat, 1951).

The fixation of atmospheric nitrogen by plants is performed non-photosynthetically; this holds also for amino acids, fatty acids, and most other organic constituents of the plant.

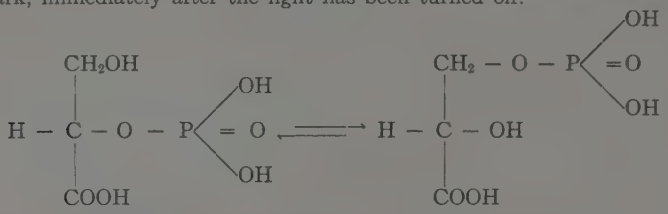
MECHANISM OF PHOTOSYNTHESIS

During the past two decades the method of chromatographic adsorption analysis, originally suggested by M. Tswett in 1906, has made great progress in technique. In form of paper chromatography it has, in recent years, become very useful in the analysis of complicated mixtures of organic substances, such as the ones found in extracts of cells after short periods of illumination. Numerous workers are using this technique in the hope of obtaining compounds which will help to elucidate the mechanism of photosynthesis; the results thus far have given a considerable amount of insight derived from the chemical structure of the substances isolated.

Ever since Liebig's time photosynthesis has been considered a process in which at least one photochemical reaction is coupled with one or more chemical reactions. The chemical steps precede or follow the photochemical reaction, and are also often called "dark reactions," "thermal reactions," or "Blackman reactions" (Blackman, 1905). They are entirely independent of irradiation, and their duration is obviously an important limiting factor for the photochemical part of photosynthesis. For the green alga *Chlorella pyrenoidosa*, Emerson and Arnold (1932) found the time required for the chemical step to be 0.02 sec. at 25° C, when light flashes of 10^{-5} sec. duration were alternating with the dark periods. Some investigators stress the necessity of studying photosynthesis in the plant's natural environment, while others favor experiments under controlled artificial conditions, which are often very different from those the plants are accustomed to. Such "unphysiological" conditions are, for instance: the change of hydrogen ion concentration in experiments with algae or aquatic plants; the use of carbon dioxide concentrations far exceeding the 0.03 percent of this gas in the atmosphere; the substitution of steady illumination by flashing light; pre-illumination of the cells before measurements of photosynthesis; or the increase of the intensity of applied radiation to very high values. Under physiological conditions, the measurements must be extended often over long periods of time in order to be significant in comparison with apparatus "errors"; but then measurements may become faulty and useless due to fluctuating reaction rates, or secondary dark reactions. At present, the tendency in photosynthesis research is to apply short exposure times (seconds or minutes), and high light intensities. Thus, the results are necessarily based on compromises; and the results refer to special conditions only, often only to one species of plants, or to a particular culture of organisms.

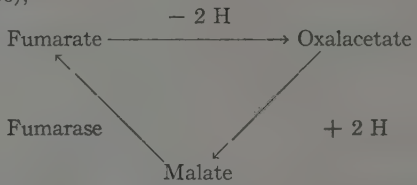
For the establishment of the reaction mechanism, the isolation and identification of intermediates become of paramount importance. In experiments of very short duration, phosphoglyceric acid has been isolated (Calvin and Benson, 1948). It is thus far the only compound, the involvement of which, in photosynthesis, may be claimed with high probability. Tracer studies at 2° C yield mainly 2-phosphoglyceric acid which is converted into 3-phosphoglyceric acid so rapidly that at 20° C the equilibrium mixture of the two substances is isolated. These findings have been confirmed and extended (Fager and Rosenberg, 1950). It was

also shown that formation of phosphoglyceric acid is the major fixation reaction in the dark, immediately after the light has been turned off.



The next most likely step in the synthesis of a hexose—the formation of a triose, or of a triose-phosphate—has not been verified so far. If phosphoglyceric acid were reduced photochemically, as has been considered (Fager, Rosenberg, and Gaffron, 1950), another light reaction besides the established splitting of the water molecule would enter the mechanism of photosynthesis. A detailed discussion of this problem can be found in Gaffron and Fager (1951), and in two recent review articles (Calvin, 1949; Benson and Calvin, 1950). The mechanism of the formation of sucrose in the plant has not yet been established.

The positive identification of organic acids, or their salts, as intermediates, is rendered difficult by the fact that the respiratory mechanism involves the production of a number of such acids. The partners in the Szent-Györgyi cycle (Szent-Györgyi, 1936),



and participants in the Krebs or "citric acid" cycle (Krebs, 1940), figure 4, have been isolated from photosynthesizing cells. The diagrams of these cycles are given here to illustrate some of the reactions superimposed on photosynthesis in general, which are very important in assimilation experiments with certain microorganisms (Gest, Kamen, and Bregoff, 1950). The Szent-Györgyi cycle acts as a hydrogen carrier in the formation and oxidation of citric acid, and in the oxidation of triose to pyruvic acid. The oxidation of one triose molecule involves one Krebs cycle, and at least three repetitions of the Szent-Györgyi cycle.

Since all photosynthesis reactions involve enzymes and enzyme systems, considerable attention has been concentrated on the study of the enzymic mechanisms of carbon assimilation (Ochoa, 1946). Vishniac and Ochoa (1951) demonstrated that the mechanism of the citric acid cycle is used after a primary light reaction which involves pyridine nucleotides. The reactions studied may be written:

$$TPNH_2 + \text{pyruvate} + CO_2 \xrightarrow{\text{light and } Mn^{++}} TPN + 1\,(-)\ \text{malate},$$

and

$$DPNH_2 + \text{pyruvate} \xrightarrow{\text{light}} DPN + \text{lactate:}$$

where TPN and DPN represent Triphosphopyridine nucleotide (Coenzyme II) and Diphosphopyridine nucleotide (Coenzyme I), respectively, and $TPNH_2$ and $DPNH_2$, the corresponding reduced forms. The observations indicate that illuminated chloroplasts are able to catalyze the over-all reaction:

$$H_2O + TPN \text{ (or DPN)} \xrightarrow{\text{light}} TPNH_2 \text{ (or } DPNH_2) + 0.5\ O_2.$$

The availability of tracer elements, especially of isotopes of carbon, has greatly stimulated investigations on the distribution or location of the tracer in the molecules of suspected intermediates before and after illumination. In experiments with *Bryophyllum*, the malic acid, which had taken up the tracer in the dark, was found to form in light a high percentage of sugar tagged in positions 3 and 4 (Varner and Burrell, 1950); results of this kind may reveal the length of the carbon chain in reaction intermediates.

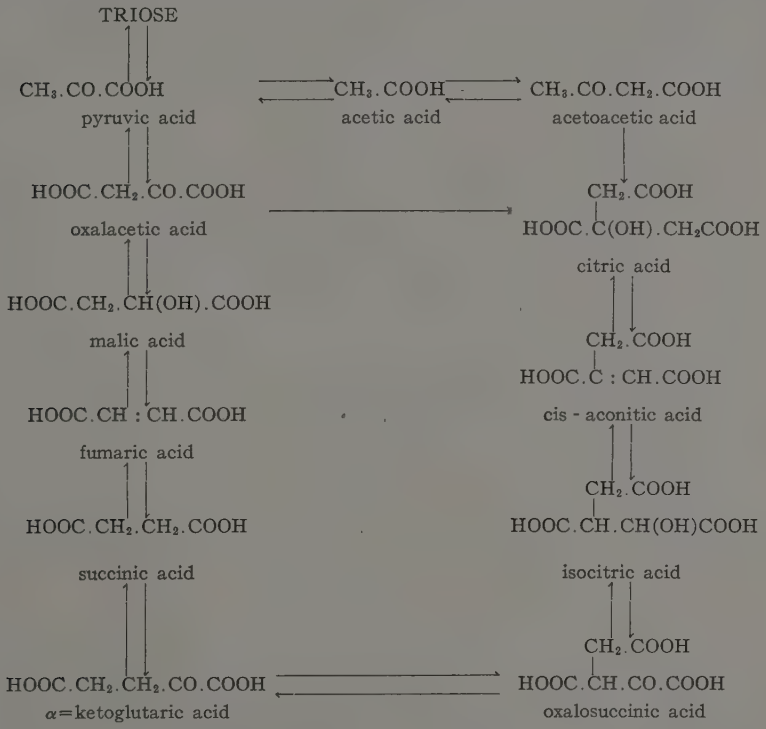


FIGURE 4. Citric Acid Cycle

MEASUREMENTS OF THE QUANTUM YIELD

Since the photosynthesis represents the conversion of light into chemical energy, the energy conversion factor of this transformation becomes of great importance. This factor, which is the measure for the efficiency of the process, is:

$$\epsilon = \frac{\text{chemical energy gained}}{\text{energy of light absorbed}} = \frac{H_c}{h\nu}.$$

The chemical energy is determined by measuring the heat of combustion, H_c, of the reaction product—in this case carbohydrate—h is Planck's constant—6.624 x 10^{-27} erg-seconds—and ν is the frequency, when light of wavelength λ (in mμ) is used:

$$\nu = 3.00 \times 10^{17}/\lambda_{m\mu}$$

For one of the structural units $[CH_2O]$, the "molar" heat of combustion (H_m) has been found experimentally to be approximately 112 kcal., or 4.69×10^{12} ergs.

Based on Planck's concept of energy quanta, Einstein postulated for photochemical processes the requirement that ideally the number of quanta (photons) of energy $h\nu$, $N_{h\nu}$ be equal to the number of molecules N, which had undergone a photochemical change by absorbing these quanta. In this case, the "quantum yield" or "quantum efficiency" would be unity.

For molar quantities, N becomes Avogadro's number—$N_A = 6.02 \times 10^{23}$ (g-mole)$^{-1}$—and for a quantum yield of one, there will be 6.02×10^{23} quanta necessary. This number of quanta corresponds to an energy of $N_A \times h\nu = N_A \times h \frac{c}{\lambda}$ ergs, that is:

$$\frac{6.02 \times 10^{23} \times 6.62^{-27} \text{ erg-sec.} \times 3.00 \times 10^{10} \text{ cm/sec.}}{\lambda_{cm}}$$

or, for λ in $m\mu$ ($= 10^{-7}$ cm):

$$\frac{6.02 \times 10^{23} \times 1.986 \times 10^{-9}}{10^{-7}} \text{ ergs} =$$

$$\frac{6.02 \times 10^{23} \times 1.986 \times 10^{-9}}{\lambda_{m\mu}} \text{ ergs} =$$

$$\frac{1.196 \times 10^{15}}{\lambda_{m\mu}} \text{ ergs} = 1 \text{ Einstein.}$$

If P moles of carbon dioxide are reduced (or P moles of oxygen evolved) in a photochemical reaction, and if the energy (I_a) of the quanta absorbed is given in Einsteins, then the quantum yield γ is:

$$\gamma = \frac{P}{I_a}.$$

This factor modifies the equation for the efficiency of the photosynthetic process, and one obtains:

$$\epsilon = \frac{H_m}{N_A h\nu} \times \gamma = \frac{4.69 \times 10^{12}}{1.196 \times 10^{15}} \times \lambda_{m\mu} \times \gamma$$

$$= 3.93 \times 10^{-3} \times \lambda_{m\mu} \times \gamma,$$

$$\text{or approximately } 4 \times 10^{-3} \times \lambda_{m\mu} \times \gamma.$$

It has been mentioned that the quantum yield γ will be unity, if one molecule of a substance, upon receiving one quantum, breaks up into component parts irreversibly. If this is not the case, then the quantum yield may be smaller or larger than one. High quantum yields are found in reactions where a single molecule absorbs one quantum and causes a sequence of reactions to start, in which many molecules are involved. The quantum yield is low when a considerable number of absorbed quanta are given off as heat or as fluorescence.

About 30 years ago Warburg and Negelein (1923) studied the photosynthetic efficiency of monochromatic light on a species of *Chlorella*, and found, for different wavelengths, quantum yields between 0.20 and 0.23. The results indicated a reaction mechanism in which four (or possibly five) quanta were required for the reduction of one mole of carbon dioxide. This finding was widely accepted. It represents, indeed, the simplest way to account for the four hydrogen atoms necessary to reduce the carbon dioxide molecule. Four individual absorption acts could easily furnish the four quanta needed. Many reinvestigations, by a great number of authors and with a variety of organisms, followed, but resulted

in values spreading from about 0.25 to 0.04 (Rothemund, 1944; Emerson and Nishimura, 1949; Moore and Duggar, 1949; Rieke, 1949; Arnold, 1949). Results with γ approximately 0.08 to 0.1, corresponding to 10 to 12 quanta, seemed to be prevailing, although they were obtained with three different and independent techniques: manometry, polarography, and calorimetry. There was agreement as to the observed phenomena, but serious disagreements in the interpretations of the experimental results. Fluorescence presents a difficult problem in this connection, and Franck (1951) gave it a great deal of attention. Transient intensity changes in fluorescence during photosynthesis were first reported by Kautsky (1934). The relationship between chlorophyll fluorescence and photosynthesis is the subject of a recent review (Wassink, 1951). Its author concludes that there is, at present, no predictable general relationship between the two. In many cases, increased intensity of fluorescence and decrease of photosynthetic yield go together. The formulation of theories on the mechanism of photosynthesis, on the basis of reported quantum yields, is, under these circumstances, a useless undertaking.

During the past four or five years, Warburg and co-workers repeated Warburg's earlier work. They found at first, in a large number of determinations of the quantum yield, a confirmation of the value 0.25 (Burk, Hendricks, Korzenovsky, Schocken, and Warburg, 1949); but later, under changed conditions, Burk and Warburg obtained for *Chlorella* in monochromatic light of one minute duration, alternating with one minute dark periods, quantum yields of 1.0 to 1.25 (Burk and Warburg, 1950; 1951). Independently in each dark period a combustion process, almost proportional to the light intensity of the light periods, took place. This combustion could be increased to about 10 to 12 times the ordinary dark respiration. It is claimed that in a novel 2-phase cycle the two energy transformations are interacting so that red light, for example, furnishes only 40 kcal., and the combustion 80 kcal. for the reduction of one mole of carbon dioxide. This ratio of 1 : 3 is interpreted to mean that three or four revolutions of the photosynthetic energy cycle suffice to allow the fixation of one mole of carbon dioxide under evolution of one mole of oxygen.

Burk and Warburg consider the one-quantum mechanism and energy cycle the solution to the long-standing quantum problem in photosynthesis (Burk and Warburg, 1951).

REFERENCES

Arnold, W. 1949. (Photosynthesis in Plants—Edited by Franck and Loomis), pp. 273–276. Iowa State College Press, Ames, Iowa.

Baur, E., K. Gloor, and **H. Künzler.** 1938. Über die Photolyse der Kohlensäure. Helv. Chim. Acta. 21: 1038–1053.

Baur, E., and **F. Niggli.** 1943. Assimilation der Kohlensäure in vitro. Helv. Chim. Acta. 26: 251–254.

Benson, A. A., and **M. Calvin.** 1950. Carbon dioxide fixation by green plants. Ann. Rev. Plant Physiol. 1: 25–42.

Blackman, F. F. 1905. Optima and limiting factors. Ann. Bot. 19: 281–295.

Burk, D., S. Hendricks, M. Korzenovsky, V. Schocken, and **O. Warburg.** 1949. Maximum efficiency of photosynthesis—a rediscovery. Science. 110: 225–229.

Burk, D., and **O. Warburg.** 1950. 1-Quanten-Mechanismus und Energie-Kreisprozess bei der Photosynthese. Naturwiss. 37: 560.

Burk, D., and **O. Warburg.** 1951. Ein-Quanten-Reaktion und Kreisprozess der Energie bei der Photosynthese. Z. für Naturforschung. 6b: 12–22.

Burk, D., and **O. Warburg.** 1951. One-quantum mechanism and energy cycle in photosynthesis. Federation Proceedings 10, Part 1, p. 169.

Calvin, M., and **A. A. Benson.** 1948. The path of carbon in photosynthesis. Science. 107: 476–480.

Calvin, M. 1949. The path of carbon in photosynthesis. VI. Jour. Chem. Education. 26: 639–657.

Dole, M., and **G. Jenks.** 1944. Isotopic composition of photosynthetic oxygen. Science. 100: 409.

Emerson, R., and **W. Arnold.** 1932. The photochemical reaction in photosynthesis. Jour. Gen. Physiol. 15: 391–420.
Emerson, R., and **W. Arnold.** 1932. The chlorophyll unit in photosynthesis. Jour. Gen. Physiol. 16: 191–205.
Emerson, R., and **M. S. Nishimura.** 1949. (Photosynthesis in Plants—Edited by Franck and Loomis), pp. 219–238. Iowa State College Press, Ames, Iowa.
Fager, E. W., and **J. L. Rosenberg.** 1950. Phosphoglyceric acid in photosynthesis. Science. 112: 617–618.
Fager, E. W., J. L. Rosenberg, and **H. Gaffron.** 1950. Intermediates in photosynthesis. Federation Proceedings. 9: 535–542.
Fischer, H., and **J. Hasenkamp.** 1935. Über die Konstitution des Farbstoffes der Purpurbakterien und über 9-Oxy-desoxophäoporphyrin a_5. Liebigs Ann. 515: 148–164.
Fischer, H., and **H. Orth.** 1943. Die Chemie des Pyrrols. Edwards Brothers, Ann Arbor, Michigan.
Franck, J., and **W. E. Loomis.** 1949. Photosynthesis in plants. The Iowa State College Press, Ames, Iowa.
Franck, J., and **H. Gaffron.** 1941. Photosynthesis: facts, and interpretations. Adv. in Enzymology. 1: 199–262.
Franck, J. 1951. A critical survey of the physical background of photosynthesis. Ann. Rev. Plant Physiol. 2: 53–86.
Gaffron, H. 1933. Über den Stoffwechsel der Purpurbakterien I. Biochem. Z. 260: 1–17.
Gaffron, H. 1935. Über den Stoffwechsel der Purpurbakterien II. Biochem. Z. 275: 301–319.
Gaffron, H. 1944. Photosynthesis, photoreduction, and dark reduction of carbon dioxide in certain algae. Biol. Rev. Cambridge Phil. Soc. 19: 1–20.
Gaffron, H., and **E. W. Fager.** 1951. The kinetics and chemistry of photosynthesis. Ann. Rev. Plant Physiol. 2: 87–114.
Gest, H., M. D. Kamen, and **H. M. Bregoff.** 1950. Studies on the metabolism of photosynthetic bacteria. *V.* Jour. Biol. Chem. 182: 153–170.
Hill, R. 1937. Oxygen evolved by isolated chloroplasts. Nature. 139: 881.
Hill, R. 1939. Oxygen produced by isolated chloroplasts. Proc. Roy. Soc. London. B 127: 192–210.
Kautsky, H., and **A. Hirsch.** 1934. Das Fluoreszenzverhalten grüner Pflanzen. Biochem. Z. 274: 423–434.
Krebs, H. A. 1940. The citric acid cycle and Szent-Györgyi cycle in pigeon breast muscle. Biochem. Jour. 34: 775–779.
Krebs, H. A. 1943. Carbon dioxide assimilation in heterotrophic organisms. Ann. Rev. Biochem. 12: 529–550.
Moore, W. E., and **B. M. Duggar.** 1949. (Photosynthesis in Plants—Edited by Franck and Loomis), pp. 239–250. Iowa State College Press, Ames, Iowa.
Ochoa, S. 1946. Enzymatic mechanisms in carbon dioxide assimilation. Currents in Biochemical Research—Chapter 12—Interscience Publishers, Inc., New York.
Peat, S. 1951. The biological transformations of starch. Adv. in Enzymology. 11: 339–75.
Rabinowitch, E. I. 1945, 1951. Photosynthesis and Related Processes. Interscience Publishers, Inc., New York.
Rieke, F. F. 1949. (Photosynthesis in Plants—Edited by Franck and Loomis), pp. 251–272. Iowa State College Press, Ames, Iowa.
Rothemund, P. 1944. Chlorophyll. Medical Physics. 1: 154–180.
Rothemund, P. 1944. Photosynthesis. Colloid Chemistry—Edited by Jerome Alexander. Vol. *V*, pp. 600–610. Reinhold Publishing Corp., New York.
Rothemund, P. 1949. Chlorophyll. Encyclopedia of Chemical Technology. 3: 871–882.
Ruben, S., W. Z. Hassid, and **M. D. Kamen.** 1939. Radioactive carbon in the study of photosynthesis. Jour. Amer. Chem. Soc. 61: 661–663.
Ruben, S., M. D. Kamen, and **W. Z. Hassid.** 1940. Photosynthesis with radioactive carbon, II. Chemical properties of the intermediates. Jour. Amer. Chem. Soc. 62: 3443–3450.
Ruben, S., M. D. Kamen, and **L. H. Perry.** 1940. Photosynthesis with radioactive carbon. III. Ultracentrifugation of intermediate products. Jour. Amer. Chem. Soc. 62: 3450–3451.
Ruben, S., M. Randall, M. D. Kamen, and **J. L. Hyde.** 1941. Heavy Oxygen (^{18}O) as a tracer in the study of photosynthesis. Jour. Amer. Chem. Soc. 63: 877–879.
Seybold, A., K. Egle, and **W. Hülsbruch.** 1941. Chlorophyll-und Carotin bestimmungen an Süsswasseralgen. Bot. Arch. 42: 239–253.
Spoehr, H. 1926. Photosynthesis. Chem. Catalog Co., New York.
Szent-Györgyi, A. 1936. Über die Bedeutung der Fumarsäure fur die tierische Gewebsatmung. III. Mitteilung. Hoppe-Seyler's Z. Physiol. Chem. 244: 105–116.
Ursprung, A. 1917. Über die Stärkebildung im Spektrum. Ber. Deutsch. Bot. Ges. 35: 44–69.
Van Niel, C. B. 1931. On the morphology and physiology of the purple and green sulfur bacteria. Arch. Mikrobiol. 3: 1.
Van Niel, C. B., and **W. Arnold.** 1938. The quantitative estimation of bacteriochlorophyll. Enzymologia. 5: 244–250.

Van Niel, C. B. 1941. The bacterial photosyntheses and their importance for the general problem of photosynthesis. Adv. in Enzymology. 1: 263–328.
Varner, J. E., and **R. C. Burrell.** 1950. Use of carbon 14 in the study of the acid metabolism of *Bryophyllum calycinum*. Arch. Biochem. 25: 280–287.
Vishniac, W., and **S. Ochoa.** 1951. Photochemical reduction of pyridine nucleotides by spinach grana and coupled carbon dioxide fixation. Nature. 167: 768–769.
Warburg, O. 1919. Über die Geschwindigkeit der photochemischen Kohlensäurezersetzung in lebenden Zellen. I. Biochem. Z. 100: 230–270.
Warburg, O., and **E. Negelein.** 1923. Über den Einfluss der Wellenlänge auf den Energieumsatz bei der Kohlensäureassimilation. Z. physikal. Chem. 106: 191–218.
Warburg, O., and **W. Lüttgens.** 1944. Experiment zur Assimilation der Kohlensäure. Naturwiss. 32: 161.
Warburg, O., and **W. Lüttgens.** 1944. Weitere Experimente zur Kohlensäureassimilation. Naturwiss. 32: 301.
Wassink, E. C. 1951. Chlorophyll fluorescence and photosynthesis. Adv. in Enzymology. 11: 91–199.
Werkman, C. H., and **H. G. Wood.** 1942. Heterotrophic assimilation of carbon dioxide. Adv. in Enzymology. 2: 135–182.

THE UTILIZATION OF THE SOLAR ENERGY THROUGH PHOTOCHEMICAL REACTIONS

JACK G. CALVERT
Department of Chemistry, The Ohio State University, Columbus 10

Many molecules and atoms absorb light and as a result undergo chemical change. Since light is one form of energy, light absorbed by a molecule results in an increase in energy of the absorbing molecule. Certain chemical changes may occur involving the molecule activated by light. If the reactions of the excited molecule are less exothermic than the energy of the light absorbed, the products of the light-initiated reaction will have a greater chemical energy than the reactants, and the over-all reaction will have resulted in the conversion of light energy into chemical energy. The trapping of the sun's light-energy by non-biological photochemical processes of this kind has been a hope of scientists for a great number of years. It is the purpose of the paper to summarize some of the fundamental considerations and problems involved in this study and to indicate the present status of research in this field.

LIGHT ABSORPTION BY MOLECULES AND ATOMS

The absorption act.—Any molecule or atom absorbing a quantum of radiant energy of wave length λ is increased in energy E by an amount, $E = hc/\lambda$, where h is Planck's constant, and c is the velocity of light. The immediate result of the absorption of light in the visible or ultraviolet range (λ = 7,000 to about 1,000 Å.) is an electronic excitation of the molecule or atom.

Reactions of the excited molecule.—Experimentation has shown that only light of wave length less than about 7,000 Å. contains sufficient energy per quantum (greater than 41 kcal./mole of quanta) to effect most chemical changes, such as breaking bonds between atoms, etc. For the ordinary forms of matter exposed to the usual intensities of sunlight the absorption of more than one quantum of light per molecule is extremely improbable and does not occur usually; this is a consequence of the very short lifetimes of the excited molecules. Roughly

fifty percent of the solar radiant energy which we receive at the earth's surface has a wave length less than 7,000 Å. and is thus sufficiently energetic to produce chemical changes in an absorbing molecule. An increase in temperature of the absorbing molecules is the predominant result of the absorption of light which is greater than 7,000 Å. in wave length.

Some of the important modes of reaction of the light activated molecule include: (*a*) fluorescence (all, or more often, a part of the energy absorbed is emitted as light); (*b*) loss of the excitation energy by collisional deactivation; (*c*) dissociation of the molecule into simpler molecules or radicals (molecular fragments); (*d*) isomerization or molecular rearrangement; (*e*) a chemical reaction between an excited molecule and a normal molecule. The only change which results in a light absorbing system which involves only reactions (*a*) and/or (*b*) is an increase in the thermal energies of the molecules. The occurrence of reactions (*c*), (*d*), and (*e*) usually results in a chemical change in the system. If light energy is absorbed by a chemical system and reaction (*a*) does not occur exclusively, then the total energy of the chemical system is increased necessarily for every such system. The increase in energy is made manifest by an increase in thermal energy of the molecules in the system and by an increase in chemical energy from the formation of energy-rich products. For the purpose of light energy conversion to chemical energy and storage of this energy, only systems involving the formation of energy-rich products are important. In this discussion such reactions will be referred to as "endothermic" photochemical reactions.

"ENDOTHERMIC" PHOTOCHEMICAL REACTIONS

The ideal reaction.—An ideal photochemical reaction for the conversion of light energy into chemical energy may have the following characteristics. (*a*) The reactant molecules absorb strongly all radiation in the visible and ultraviolet. In other words, the reactant is black or dark in color. (*b*) A given chemical reaction follows the absorption of each quantum of light with perfect efficiency. Reactions of fluorescence and collisional deactivation are unimportant. (*c*) The over-all chemical change in the reaction system involves a large increase in free energy. (*d*) The products formed absorb no light in the visible or ultraviolet region; therefore they are colorless. (*e*) The exothermic reaction of the products to reform the reactants is extremely slow under ordinary conditions but this or some other reaction involving the products proceeds readily under special controlled conditions (e.g., at an elevated temperature or in a battery) to liberate thermal or electrical energy.

A measure of the efficiency of energy conversion.—In our discussion of the "endothermic" photochemical reactions it will be useful to define and use a quantity, Q, which provides a measure of the percent efficiency of the light energy conversion to chemical energy.

$$Q = (100)\ (\Delta F^\circ_{298})\ (\Phi_A)/E\lambda),$$

where ΔF°_{298} is the standard free energy increase for the over-all chemical reaction (kcal. mole of a given product A formed), Φ_A is the quantum yield of the given product A (molecules of A formed/quantum of light absorbed by the reactant), and E_λ is the energy of the absorbed light of wave length λ (E_λ in kcal. mole = 2.86×10^5 λ in Å.). Q can give at best only an approximate indication of the efficiency of energy conversion for several reasons: (*a*) the photochemical reactions for which data are available were not studied with reactants and products in concentrations corresponding to the reference states used for ΔF°_{298} calculations; (*b*) the quantum yield data are usually maximum values obtained only under special conditions (certain wave length region, low percentage reaction, etc.); (*c*) the effects of product interference by absorption and subsequent decomposition or reaction are not considered; (*d*) a great many "endothermic" photochemical

reactions are reversible; a definite photostationary concentration of reactants and products is reached, and then concentrations remain unchanged for a given temperature, light intensity, and initial concentration of reactants or products. The values of the photostationary concentrations are important in determining the usefulness of a given "endothermic" photochemical reaction for energy conversion. Unfortunately this type of data is not available for most reactions. The factors stated cause the estimate of efficiency of energy conversion, Q, to be higher than actually obtainable experimentally. Regardless of the approximate nature of Q we will find that it is a useful guide to our discussion.

Photosynthesis in vitro.—Many attempts have been made to accomplish photosynthesis in the laboratory without the help of living cells. A general over-all reaction which will serve to illustrate photosynthesis may be written: $nH_2O + nCO_2 \longrightarrow (CH_2O)n + nO_2$, where n is some whole number. The reaction is highly endothermic; about 110 kcal. of energy is evolved when the organic product material containing one gram atom of carbon is burned in air. Energy considerations and the transparency of water and carbon dioxide to all wave lengths of visible and near ultraviolet light make impossible the occurrence of this reaction involving only pure water, carbon dioxide, and sunlight. The very short ultraviolet wave lengths (where absorption and energies are more

TABLE 1

Some far ultraviolet "endothermic" photochemical reactions.

OVER-ALL CHEMICAL REACTION	EFFECTIVE WAVE LENGTHS, Å	QUANTUM YIELD (product)	$\Delta F°_{298}$ kcal./mole	Q PERCENT EFFICIENCY	INVESTIGATORS
(1) $3/2\ O_2 \longrightarrow O_3$	<1751 (weak absorption)	2.0 (O_3)	32.4	40.5	Warburg (1914) Vaughan, Noyes (1930)
	2070	2.0		47.0	
	2537	1.1		31.8	
(2) $CO_2 \longrightarrow CO + \frac{1}{2}\ O_2$	<1692	1.0 (CO)	61.4	36.4	Groth (1937)
(3) $H_2O \longrightarrow H_2 + \frac{1}{2}\ O_2$	<1800	(small)	54.5		Groth, Suess (1938) Terenin, Neuimin (1934)
(4) $CO + H_2 \longrightarrow CH_2O$	<1470	0.5(CH_2O)	6.6	1.7	Groth (1937)
(5) $NH_3 \longrightarrow \frac{1}{2}\ N_2H_4 + \frac{1}{2}\ H_2$	<2138	0.5(H_2)	17.1 ($\Delta H°_{298}$)	12.8	Review of work by Noyes, Leighton (1941)
(6) $CH_4 \longrightarrow \frac{1}{2}H_2 + \frac{1}{2}\ C_2H_6$ or	<1450				Groth (1937)
	1295	0.5(H_2)	6.9	3.1	Groth, Laudenklos (1936)
$CH_4 \longrightarrow H_2 + \frac{1}{2}\ C_2H_4$			18.4	4.2	Leighton, Steiner (1936)

favorable for the reaction) may cause the occurrence of this or related reactions, but its occurrence is questionable even under these conditions (Rabinowitch, 1945). It is not inconceivable that we may be able to realize the reaction *in vitro* through the proper choice of sensitizer, catalysts, etc., after our knowledge of the mechanism of photosynthesis *in vivo* has been greatly increased.

Known "endothermic" photochemical reactions.—The inexperienced investigator in this field may be surprised to find that the great majority of known photochemical reactions are accompanied by an over-all decrease in free energy; i.e., a normally slow, exothermic reaction is promoted by light, and the energy of the absorbed light plus that due to the exothermal nature of the reaction ultimately appears as an increase in velocity of the product molecules. However, there are a relatively small number of "endothermic" photochemical reactions which have been reported. It is probably unnecessary to point out that no system is now known which is at all comparable to the "ideal reaction" described in a preceding section. The "endothermic" photochemical reactions may be divided

into two groups for the purposes of our discussion: the reactions occurring on the absorption of the far ultraviolet light ($\lambda < 2{,}500$Å.), and those reactions occurring on the absorption of visible or the near ultraviolet radiation.

The far ultraviolet "endothermic" photochemical reactions.—A few of the "endothermic" photochemical reactions which occur on absorption of light in the far ultraviolet are summarized in table 1. Only the over-all chemical change which takes place is listed in each case; for our very limited considerations it is an unnecessary complication to describe the detailed mechanism of the reaction steps which lead to the over-all reactions. The very short wave lengths of light which promote these chemical changes are absent in sunlight striking the earth as a result of the occurrence of some of these and other photochemical reactions in the upper atmosphere of the earth. The distribution of solar radiant energy reaching the earth's surface at Cleveland on a clear summer day when the atmospheric pressure is 1.07 atm. has been calculated by Forsythe and Christison (1930). A portion of their data is reprinted in table 2. There are minor variations in this distribution with changes in season, pressure, etc. Since light energy must be absorbed before a chemical change can be effected photochemically, the direct occurrence of the reactions of table 1 in sunlight incident at the earth's surface is impossible. However it is probable that these and other "endothermic" photochemical reactions were important in the prebiological chemistry of the earth.

TABLE 2

*Distribution of radiant energy from the sun on the earth's surface at Cleveland**

WAVE LENGTH REGION, Å.	PERCENTAGE OF THE TOTAL ENERGY
2900–3100	0.019
Less than 3250	0.21
Less than 3500	1.0
Less than 4000	3.8
4000–7600	43.9
Greater than 7600	52.3

* Forsythe, W. E., and F. Christison (1930).

The near ultraviolet and visible "endothermic" photochemical reactions.—In table 3 several "endothermic" photochemical reactions which are initiated by the absorption of visible or ultraviolet light are summarized. Reactions (7), (8), (9), (10), and (15a) occur only in the ultraviolet region of light; since this region is practically absent from sunlight (table 2), these reactions will remain unimportant for energy conversion on the earth unless some photochemical sensitizer for the longer wave lengths is found for these systems.

It should be noted that the possibility exists of extending the useful wave length region of a given reaction to a position which is more compatible with the energy distribution of the sun. For example, Blacet (1952) has proposed tentatively that ozone formation [reaction (1) of table 1] at the earth's surface may result from the primary absorption of light by nitrogen dioxide (effective absorption region, $\lambda < 4{,}350$ Å.) according to the following sequence of reactions:

$$NO_2 + h\nu \longrightarrow NO + O$$
$$O + O_2 \longrightarrow O_3$$
$$NO + O_2 \longrightarrow NO_3$$
$$NO_3 + O_2 \longrightarrow NO_2 + O_3$$

($h\nu$ represents the energy of a quantum of light of frequency, ν.) If these reactions occur, the over-all change resulting from light absorption by the nitrogen dioxide is given by: $3O_2 \longrightarrow 2O_3$. Thus a change which is effected as a result of direct light absorption by a reactant only at the very short wave lengths may be made to occur indirectly by a sequence of reactions initiated by visible light absorption by a sensitizer.

TABLE 3

Some ultraviolet and visible "endothermic" photochemical reactions

OVER-ALL CHEMICAL REACTION	EFFECTIVE WAVE LENGTHS, Å.	QUANTUM YIELD (product)	$\Delta F°_{298}$, kcal./mole	Q PERCENT EFFICIENCY	INVESTIGATORS
(7) $HBr \longrightarrow \frac{1}{2} Br_2 + \frac{1}{2} H_2$	<2537	1.0 (Br_2)	12.5	22.2	Warburg (1916)
	2090	1.0		18.3	
(8) $SO_3 \longrightarrow \frac{1}{2} O_2 + SO_2$	<2760	(small)	16.2		Kornfeld (1937)
(9) $COCl_2 \longrightarrow CO + Cl_2$	<2750	0.9(CO)	16.3	14.0	Montgomery and
	2537			13.1	Rollefson (1934)
(10) $NO^-_3 \longrightarrow NO^-_2 + \frac{1}{2} O_2$	<3350	0.014(NO^-_2)	18.0	0.20	Warburg (1918)
(water solution)	2804	0.024		0.42	Villars (1927)
	2700	0.07		1.2	
	2540	0.30		4.8	
(11) $NO_2 \longrightarrow NO + \frac{1}{2} O_2$	<4350	0.046(NO)	9.0	0.6	Dickinson, Baxter (1928)
	4050	0.36		4.6	
	3660	0.77		8.8	
(12) $NOCl \longrightarrow NO + \frac{1}{2} Cl_2$	<6370	2.0(NO)	4.9	21.8	Bowen, Sharp (1925)
	3650	2.0		12.5	Kistiakowsky (1930)
(13) $2Fe^{+2} + I^-_3 \longrightarrow 2Fe^{+3} + 3I^-$	<5460	2.0(Fe^{+3})	9.4	9.0	Kistiakowsky (1927)
(water solution)	3660			6.0	
(14) $I_2 + NO^-_2 + H_2O$					
$\longrightarrow NO^-_3 + 2HI$	<5790				
(water solution)	4360	0.1(NO^-_3)	13.8	2.1	Durrant, *et al.*, (1938)
(15a) $Fe^{+2} + H_2O \longrightarrow \frac{1}{2} H_2 +$					
$Fe^{+3} + OH^-$	<2900	0.05(H_2)	36.2	3.7	Potterill, *et al.*, (1936)
(water solution)					
b) $Fe^{+2} + H^+ \longrightarrow Fe^{+3} +$					
$\frac{1}{2} H_2$ ($HClO_4$ solution)	2537	0.1(H_2)	17.1	3.0	Heidt, DesRoches
	(5900?)				(1952)
(16) 2 Anthracene $\longrightarrow$ Dianth-					
racene	<3800		15.6		Weigert (1927)
(organic solution)	3660	0.25(Dian.)	($\Delta H°_{298}$)	5.0	
	3130	0.23		3.9	
(17a) $AgCl(s) \longrightarrow Ag(s) + \frac{1}{2} Cl_2$	<4050	1.0(Ag)	26.2	37.1	Luther (1899)
					Hartung (1922)
b) $AgBr(s) \longrightarrow Ag(s) + \frac{1}{2} Br_2$	<4600	1.0(Ag)	22.9	37.0	Hartung (1924)
c) $AgI(s) \longrightarrow Ag(s) + \frac{1}{2} I_2$	<4400	1.0(Ag)	15.8	24.3	Hartung (1926)
d) $AgCl + \frac{1}{2} H_2O \longrightarrow Ag +$					
$HCl + \frac{1}{4} O_2$	<4050	(1.0?)	23.2	(32.9)	Baur (1908)
(water suspension)					Baur, Rebmann (1921)
(18) $H_2O + \frac{1}{2} O_2 \longrightarrow H_2O_2$	<4000		25		Baur, Neuweiler (1927)
(water suspension of ZnO)	3660	0.09(H_2O_2)		2.9	Kettering Research
	3130	0.13		3.6	Group (1952)

There are few known gas phase reactions which offer promise as energy converters. The reactions (11) and (12) have reasonably large Q values and fairly satisfactory absorption. The reverse thermal reactions are termolecular in each case, but even so the rates of reaction are too rapid at ordinary pressures and temperatures to make practical the storage of the energy-rich products without separation.

A few homogeneous solution reactions appear to satisfy some of our requirements for the ideal "endothermic" photochemical reaction. Reactions (13),

(14), and (15b) illustrate this type. One of the most promising of these is reaction (15b), although product absorption becomes serious at small percentages of conversion at some wave lengths. Preliminary results of Heidt and DesRoches (1952) have indicated that the evolution of hydrogen occurs even when the solution of iron salt in perchloric acid is exposed to yellow light.

The useful spectral range of reaction (16) is limited to wave lengths less than 3,800 Å. (less than two percent of the total sunlight energy), but at these wave lengths the conversion of anthracene to dianthracene may be effected quite efficiently and continuously without serious interference from light sensitive products; the slightly soluble dianthracene separates during exposure of a solution of anthracene in some organic solvents.

It appears that a very important contribution to the problem of light to chemical energy conversion has been made recently by Heidt (1951). He reported that a sensitized photodecomposition of water [reaction (3) of table 1] occurs in the perchloric acid solutions of ceric and cerous perchlorates. The efficiencies of this "endothermic" photochemical reaction were very low and only light of wave length 2,537 Å. was used in the experiments described. However, Heidt stated that no attempt has been made yet to increase this efficiency (by the proper choice of sensitizer concentration, etc.), and also it is logical to assume that wave lengths longer than 2,537 Å. which are absorbed by the cerium ions will be effective in promoting the reaction. The ease with which the energy rich products, hydrogen and oxygen, can be stored and used as a high energy fuel when desired adds to the great attractiveness of this system.

Several heterogeneous reactions involving solids are given in table 3. The silver halide decomposition reactions (17a), (17b), and (17c) which are important in photographic processes may prove useful as energy converters.

Hydrogen peroxide formation by reaction (18) involves the light activation of zinc oxide crystals suspended in a water solution. The absorption of zinc oxide limits the reaction to wave lengths comprising only four percent of the sunlight energy, and the light energy in the wave length region utilized is converted with relatively low efficiency. However, this system has an inherent appeal as an energy converter. It appears that the highly endothermic reaction (18) is promoted from readily available reactants; the energy rich product is transparent to sunlight; the product can be stored conveniently; and the reverse reaction of peroxide decomposition can be catalyzed at will to release energy. In view of these considerations, several detailed reinvestigations of this system have been initiated recently (Kettering Research Foundation, 1952).

SUMMARY

Although no ideal chemical reaction system for the conversion of the sun's radiant energy to chemical energy is now known, several reactions under study are sufficiently attractive to give encouragement and hope for a possible ultimate solution to this problem.

LITERATURE CITED

Baur, E. 1908. Über ein Modell der Kohlensäureassimilation. Z. physik. Chem. 63: 683–710.
Baur, E., and **A. Rebmann.** 1921. The photolysis of water. Helv. Chim. Acta 4: 256–262.
Baur, E., and **C. Neuweiler.** 1927. Photolytic formation of hydrogen peroxide. Helv. Chim. Acta 10: 901–907.
Blacet, F. E. 1952. Photochemistry in the lower atmosphere. Ind. Eng. Chem. 44: 1339–1342.
Bowen, E. J., and J. F. Sharp. 1925. The photochemical decomposition of nitrosyl chloride. Jour. Chem. Soc. 127: 1026–1028.
Dickinson, R. G., and **W. P. Baxter.** 1928. The quantum yield in the photochemical decomposition of nitrogen dioxide. Jour. Amer. Chem. Soc. 50: 774–782.
Durrant, G. G., R. O. Griffith, and **A. McKeown.** 1938. The photo-reactions of nitrites with iodine. Trans. Faraday Soc. 34: 389–410.

Forsythe, W. E., and **F. Christison.** 1930. Ultraviolet radiation from the sun and heated tungsten. Jour. Opt. Soc. Amer. 20: 396–410.
Groth, W., and **H. Laudenklos.** 1936. The mechanism of photochemical methane decomposition. Naturwissenschaften, 24: 796.
———. 1937. Photochemical experiments in the Schumann ultraviolet. III. Quantum yield of photochemical gas reactions in wave length regions below 1500 Å. Z. physik. Chem. B37: 307–314.
———. 1937. Photochemical experiments in the Schumann ultraviolet. IV. The photochemical oxidation of carbon monoxide and carbon monoxide as a sensitizer. Z. physik. Chem. B37: 315–322.
———. 1937. Photochemical experiments in the Schumann ultraviolet. V. The photochemical decomposition of methane. Z physik. Chem. B38: 366–380.
———, and **H. Suess.** 1938. The photochemistry of the atmosphere. Naturwissenschaften 26: 77.
Hartung, E. J. 1922. The action of light on silver bromide. Jour. Chem. Soc. 121: 682–691.
———. 1924. Studies with the microbalance. Part I. The photochemical decomposition of silver bromide. Jour. Chem. Soc. 125: 2198–2207.
———. 1926. Studies with the microbalance. Part IV. The photochemical decomposition of silver iodide. Jour. Chem. Soc. 1926: 1349–1354.
Heidt, L. J. 1951. Non-biological photosynthesis. Proc. Amer. Acad. Arts Sciences 79: 228–233.
Heidt, L. J., and **J. C. DesRoches.** 1952. Conversion of light into chemical energy by means of the photochemical production of hydrogen gas by light absorbed by ferrous ions. Unpublished paper presented July, 1952, to the C. F. Kettering Research Foundation, Dayton, Ohio.
Kettering, C. F., Research Foundation. 1952. Unpublished papers on hydrogen peroxide formation at light activated zinc oxide surfaces. Presented July, 1952, to the C. F. Kettering Research Foundation, Dayton, Ohio, by J. G. Calvert, W. MacNevin, G. T. Rankin, and T. R. Rubin (The Ohio State Univ.); J. P. Holmquist, C. B. Vail, and L. White, Jr. (S. Research Inst.); D. Trivich (Wayne Univ.); H. Tanner (Dayton laboratory of the Kettering Research Foundation); W. Culbertson, Jr., C. R. Hurley, and L. J. Pflug (Univ. of Denver).
Kistiakowsky, G. B. 1927. The action of light on the ferrous-ferric:iodine-iodide equilibrium. Jour. Amer. Chem. Soc. 49: 976–979.
Kistiakowsky, G. B. 1930. Photochemical decomposition of nitrosyl chloride. Jour. Amer. Chem. Soc. 52: 102–108.
Kornfeld, G. 1937. Primary process of the photodissociation in sulfur trioxide. Trans. Faraday Soc. 33: 614–617.
Leighton, P. A., and **A. B. Steiner.** 1936. Photochemical decomposition of methane. Jour. Amer. Chem. Soc. 58: 1823.
Luther, R. 1899. Studies of reversible photochemical processes. Z. physik. Chem. 30: 628–680.
Montgomery, C. W., and **G. K. Rollefson.** 1934. The photochemical decomposition of phosgene. Jour. Amer. Chem Soc. 56: 1089–1092.
Noyes, W. A., Jr., and **P. A. Leighton.** 1941. The Photochemistry of Gases. pp. 370–382. Reinhold Publishing Corp., New York, N. Y.
Potterill, R. H., O. J. Walker, and **J. Weiss.** 1936. Electron affinity spectrum of ferrous ion in aqueous solution. Proc. Roy. Soc. London A156: 561–570.
Rabinowitch, E. 1945. Photosynthesis, Vol. I, pp. 81–99. Interscience publishers. New York, N. Y.
Terenin, A., and **H. Neuimin.** 1934. Photodissociation of molecules in the Schumann ultraviolet. Nature 134: 255.
Vaughan, W. E., and **W. A. Noyes, Jr.** 1930. Photochemical studies. XI. Quantum efficiency of ozone formation in the fluorite region. Jour. Amer. Chem. Soc. 52: 559.
Villars, D. S. 1927. The photolysis of potassium nitrate. Jour. Amer. Chem. Soc. 49: 326–337.
Warburg, E. 1914. Energy conversion in photochemical processes in gases. IV. Influence of wave length and pressure on photochemical ozonization. Sitzber. kgl. preuss. Akad. Wiss. 1914: 872–885.
———. 1916. Energy conversion in photochemical processes in gases. VI. Photolysis of hydrobromic acid. Sitzber. kgl. preuss. Akad. Wiss. 1916: 314–329.
———. 1918. Energy conversion in photochemical processes in gases. VIII. The photolysis of aqueous solutions and the photochemical equivalence law. Sitzber. preuss. Akad., Math.-Phys. Klasse. 1918: 1228–1246.
Weigert, F. 1927. The mechanism of photochemical polymerization of anthracene. Naturwissenschaften. 15: 124–126.

PHOTOVOLTAIC CELLS AND THEIR POSSIBLE USE AS POWER CONVERTERS FOR SOLAR ENERGY

DAN TRIVICH

Department of Chemistry, Wayne University, Detroit, Michigan

There are a number of possible methods by which one may convert solar energy into other more useful forms of energy. In the past and currently, man has made most use of chemical energy as an intermediate form, either through the growing in sunlight of food plants and trees for wood or the collection of stored remnants of such material such as coal, oil, and gas. The useful work is obtained by the the proper release of the chemical energy as in animal bodies or in steam engines. A particularly large proportion of our work requirements of energy is obtained by further conversion of the energy from the steam engine into electrical energy because of the convenience of distribution. Because of this, the possibility of direct conversion of solar energy into electrical power is a particularly fascinating one. While not practical yet, from a competitive cost standpoint, possible methods for doing this already exist.

Devices which show an electrical response to light are called photoelectric cells. This paper surveys the constitution and properties of certain types of photoelectric cells and considers the potentialities of such cells as possible converters of solar energy.

One might classify photoelectric cells as photoemissive, photoconductive, or photovoltaic. Photoemissive cells, or phototubes as they are sometimes called, contain two electrodes in an evacuated glass envelope. One of the electrodes has a special photosensitive surface which releases electrons when the proper light falls on it. By application of a potential difference between the two electrodes, an electron current passes which continues through the external circuit. In the gas-filled phototube, a variation of the vacuum phototube in which a low gas pressure replaces the vacuum, the photoelectrons ionize the gas, resulting in a larger current. Phototubes have been very extensively developed commercially for control and measurement purposes.

Photoconductive cells consist of a special solid material, such as selenium, lead, or thallous sulfide, placed between two electrodes. Light falling on the solid causes a large decrease in the resistance of the cell so that with a fixed potential difference applied between the electrodes an increased current passes. Such cells are also used for control and measurement purposes to a limited extent, particularly for the infra-red portion of the spectrum where most phototubes do not respond.

Both photoemissive and photoconductive cells require an external source of potential, that is, an external source of energy for driving the electrons through the circuit. In such cells, the light merely controls the electrical response rather than generates it. Hence, these cells are not useful for the conversion of solar energy to electrical energy. However, the photovoltaic cells respond to light by generating an electromotive force between two electrodes, which can be used to force a current through an external circuit. Thus, photovoltaic cells require no external battery, the source of energy being the light itself. Because of this characteristic, photovoltaic cells can, in principle, convert solar energy directly into electrical power.

There are two general types of photovoltaic cells, the "wet" and the "dry" types. The "wet" type was discovered first, but the mechanism is still not well understood. A review of this type of cell was given by Copeland, Black, and Garrett (1942). The cells are less stable than the "dry" type, perhaps inherently so, and have therefore received less attention. This paper is restricted to the "dry" type of cell, so that any further reference to photovoltaic cells will be understood to apply to the "dry" type.

The Ohio Journal of Science 53(5): 300, September, 1953.

Photovoltaic cells are also known by the names "barrier layer," "sperrschicht," "solid," "rectifying," "blocking layer," "valve," and "rectifying layer." The best known cells of this type are the selenium and the cuprous oxide cells. The early history of such cells is given by Lange (1938).

THE PHYSICAL CONSTITUTION OF PHOTOVOLTAIC CELLS

Photovoltaic cells in their most common form, such as those used in photographic exposure meters, consist of discs about two inches in diameter and less than one-eighth inch thick.

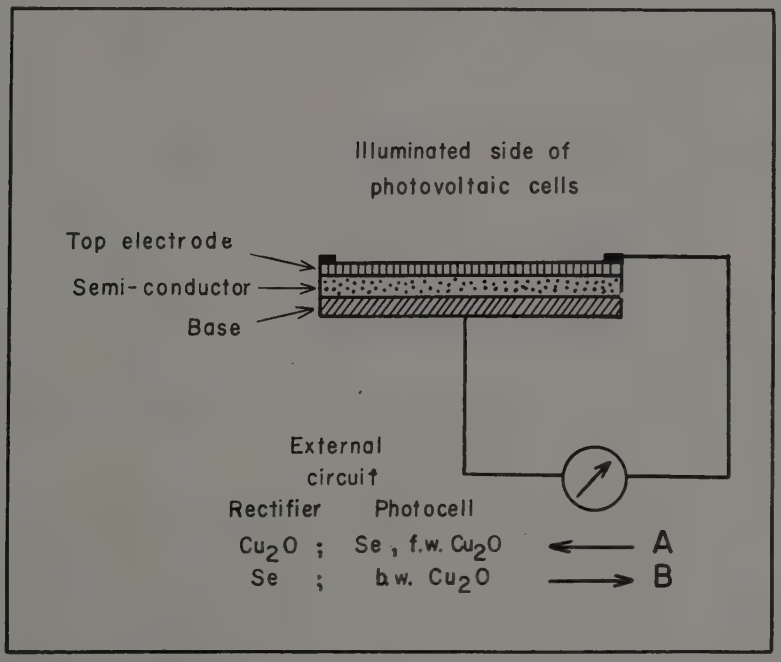


FIGURE 1. Schematic diagram for barrier-layer rectifiers and photovoltaic cells. For photovoltaic cells, the top electrode is either transparent or perforated. A is the direction for easy electron flow for cuprous oxide rectifiers and B, for selenium rectifiers. For photovoltaic cells, the direction of electron flow is A for selenium and front-wall cuprous oxide cells, and B is the direction for back-wall cuprous oxide cells.

Selenium photovoltaic cells are prepared by melting selenium on a sheet of iron, solidifying and recrystallizing the selenium, and applying a top electrode (Preston, 1950). The construction of such a cell may be deduced from the diagram in figure 1. The cell is illuminated through the top electrode, which is, therefore, either perforated or thin enough to be transparent and is often applied by vacuum evaporation or sputtering.

Such a cell will have rectifying properties (Henisch, 1949; Preston, 1950) as well as photovoltaic properties although the details of preparation differ from best attainment of either. In rectification—the conversion of alternating current into direct current—the current passes much more readily from top to bottom within the cell. The conduction is known to be electronic and not ionic, since no electrolysis occurs; and the direction of easy electron flow is from the base into the

selenium to the top electrode. The current passed at any given voltage is proportional to the area of the plate. The resistance in the forward direction drops rapidly in the forward direction with increasing voltage and increases sharply to a maximum in the reverse direction. At a potential of one volt across a typical selenium rectifier cell, the current passing the cell is of the order of several hundred milliamperes per square centimeter in the forward direction and several hundredths of a milliampere in the reverse direction.

On illumination of a selenium photovoltaic cell, a current passes from the selenium to the top electrode—the electrons flow from the top electrode into the selenium. As shown in figure 1, this is in the high resistance direction and opposite to the direction of easy electron flow for the rectifier. The photocurrent is also proportional to the area of the cell (an important fact in the consideration of energy conversion).

The cuprous oxide photocell, or rectifier, is usually prepared by heating a copper disc to about 1000° C. in the presence of air or oxygen. The surface of the copper is thus converted to cuprous oxide overlaid by cupric oxide. A concentration gradient of oxygen exists in the oxide layers, the concentration on the outside being sufficient to form the cupric oxide, while on the inside only cuprous oxide is formed with a gradient of stoichiometrically excess oxygen. This excess of oxygen is important in determining the conductivity and other properties of the cells. It is common in such cells that the properties are sensitive to traces of impurities, requiring the presence of certain beneficial ones and the absence of certain detrimental ones. The cupric oxide overlay is undesirable merely because of its high resistance and is removed. With a pressed top metal contact, a rectifier is obtained with the direction of easy electron flow being from the copper base into the cuprous oxide, as indicated in figure 1. With a perforated top electrode or thin evaporated electrode, a photovoltaic cell is obtained with the direction of electron flow in the high resistance direction, as in the case of the selenium cells; this direction, in the case of the cuprous oxide cell, being from the cuprous oxide into the copper base electrode. Such a cell, called a back-wall cell, is also represented in figure 1.

However, if the top metal electrode is applied by a sputtering technique, a cell of quite different properties is obtained; the principal difference being that the photocurrent now has the electrons flowing from the cuprous oxide toward the top electrode. The cells of this type are called front-wall cells. In addition, these cells produce higher photocurrents and have different spectral sensitivity curves, as compared with the back-wall cells.

According to the theories of Schottky (1942) and of Mott (1948) and others, the physical assemblies described owe their rectifying and photovoltaic properties to the existence of a "barrier layer", at or near the contact of one of the electrodes, to the cuprous oxide or selenium. In the case of the back-wall cuprous oxide photocell and rectifier, the barrier layer lies at the interface at which the cuprous oxide joins the base copper electrode. In the selenium cells and the front-wall cuprous oxide photocell, the effective barrier layer lies at the top electrode interface. The barrier layer acts as a high resistance in the reverse direction for the rectifiers. A satisfactory explanation of the barrier layer and the theories of rectification and photovoltaic action requires an examination of some of the modern theories of the solid state, and, in particular, of a special class of solids —the semiconductors.

SOLIDS AND SEMICONDUCTORS

An isolated atom can be described as a massive, positively charged nucleus surrounded by a number of negatively charged electrons possessing definite energies and defined by a set of characteristic quantum numbers. The Pauli principle states that no two electrons can be identical in all of their quantum numbers, or,

stated in another way, no two electrons can occupy precisely the same energy state. However, some of the energy states can have the same energy, i.e., they are degenerate. According to the customary notation, sodium is described by an electronic structure $1s^2\ 2s^2\ 2p^6\ 3s$. While the electrons do not occupy precise orbits, the energy levels of the electrons in isolated atoms are fairly definitely fixed, as suggested for the 3s and 3p orbits for sodium in the left of figure 2A.

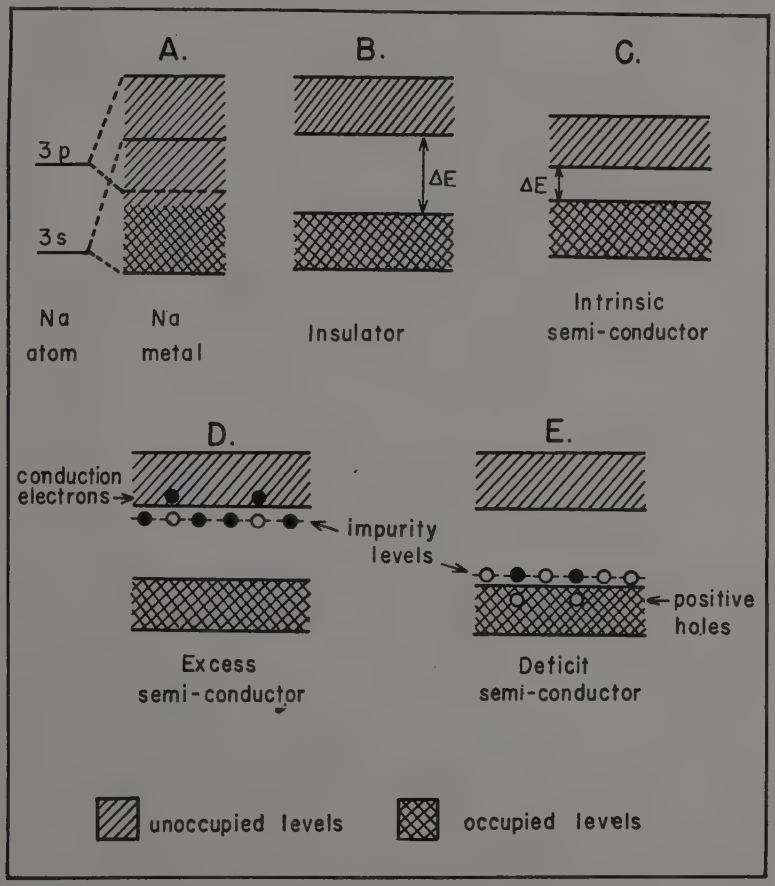


FIGURE 2. Schematic representation of energy levels for electrons in different systems.

When isolated atoms are brought together to form solids, three dimensional arrangements of the atoms result with the outer electrons rearranging themselves into more stable arrangements to contribute the necessary chemical binding. In some cases this requires a transfer of electrons from one type of atom to another creating ions, so that the force of binding arises from the coulombic attraction between the oppositely charged ions. This is true for sodium chloride, cuprous oxide, and many others. In some other types of compounds, the electrons are shared between adjoining atoms, so that the binding arises from highly directional

localized covalent bonds. The arrangements of the atoms in solids depend also on stoichiometrical relationships, relative sizes of the atoms or ions and other factors; and are commonly studied by X-ray diffraction methods. Cuprous oxide has a characteristic ionic structure; selenium can exist in several structures, among them a chain arrangement of atoms held by covalent bonds; and germanium and silicon possess the diamond structure in which each atom is held by four others by covalent bonds in a tetrahedral arrangement.

The energy situation in a solid differs somewhat from that in the isolated atoms. The inner electrons are relatively undisturbed by bringing the atoms together, but the energy levels of the outer electrons are separated and broadened into bands, as shown for sodium in figure 2A. The electrons occupy in general the lowest energies possible, again with the Pauli restriction of no more than one electron per state. At room temperature relatively few electrons are above their lowest possible energies. In the formation of solid sodium chloride, the band arising from 3p levels of chlorine is lower than the 3s band from sodium, and since an additional electron can be accommodated per chlorine atom, electrons are transferred from sodium to chlorine, giving rise to an ionic solid.

The ability of a solid to conduct electric current electronically depends not only on having electrons available, but also on having easily accessible vacancies (energy levels) for them to move into. Good conductors (i.e., metals) result when a band of closely spaced energy levels is only partly filled with electrons, so that nearby unfilled levels are assured, as shown in the energy diagram of figure 2A. Another variation of the metallic structure is obtained when there are enough electrons to fill the band completely, but another band which might have been expected to be empty overlaps the first band.

Even when a completely filled band is separated from a completely empty band, there is the possibility of thermal excitation of electrons—the fraction of thermally excited electrons being of the order $\exp(-\Delta\epsilon/kT)$. When $\Delta\epsilon$ is large compared to kT, the fraction is very small so that an extremely poor conductor (i.e. an insulator) is obtained. This is pictured in figure 2B. If $\Delta\epsilon$ is not large compared to kT, an intrinsic semiconductor is obtained, as in figure 2C. The conductivity, which is the reciprocal of the resistivity, depends upon the number of conducting electrons which in turn depends upon the factor $\exp(-\Delta\epsilon/kT)$. A usual manner of expressing the experimental data for such systems involves plotting the logarithm of the conductivity or resistivity against the reciprocal of the absolute temperature, since this results in a straight line plot over a considerable range of temperatures.

The electrical properties of semiconductors can be very profoundly altered by the presence of the proper impurities or sometimes by a slight departure from the stoichiometrically correct composition. The reason for this is that the impurities introduce new energy levels near the bands belonging to the semiconductor. Two situations are possible. In one case, as illustrated in figure 2D, the impurity levels containing electrons lie very close to an empty band of the semiconductor. Since the energy gap is small, an appreciable number of electrons is excited into the empty band, which is called a conduction band because the electrons are free to conduct there. The resulting semiconductor is said to be an excess semiconductor or an n-type (negative), since its conduction is primarily due to these excess electrons.

In another type of semiconductor, the impurities introduce empty levels near the topmost completely filled band of the semiconductor, as shown in figure 2E. Excitation of electrons from the filled band to the empty impurity levels leaves vacancies or "positive holes" in the previously filled band, so that conduction is now possible in this band. While the conduction is still by means of electrons, another way of viewing the situation is that when a conducting electron jumps into a vacancy, the vacancy moves in the opposite direction. Hence, by this view,

the conduction is effected by means of positive holes moving in the direction of of classical positive electricity. Such semiconductors are known as deficit or *p*-type (positive) semiconductors. Cuprous oxide and selenium are both usually deficit semiconductors.

While in principle, any intrinsic semiconductor can be made into an excess or deficit semiconductor, the usual methods of preparation lead to one or the other preferentially. Cuprous oxide is a deficit semiconductor because the excess of oxygen which exists in the cuprous oxide acts as an electron acceptor, thus creating the positive holes. On the other hand, heating zinc oxide in air tends to drive off some of the oxygen leaving a stoichiometric excess of zinc which serves as an electron donor, thus creating an excess semiconductor. A chemical representation of the situation might be given by:

$$2\,ZnO \longrightarrow 2\,Zn^{++} + O_2 + 4e$$

In the case of the cuprous oxide, the positive hole might be represented by a cupric ion or perhaps an oxygen with a single negative charge. Impurity atoms can occupy either interstitial positions in the crystal lattice or perhaps a regular lattice position with a compensating imperfection elsewhere.

The semiconductors, germanium and silicon, have been extensively studied recently, because of their usefulness in radar detectors and in transistors. Both of these elements have four electrons in their outer orbits as does carbon; and their solid forms assume the diamond structure in which each atom is bound to four other atoms by covalent bonds. Atoms with five outer electrons, such as phosphorus, arsenic, or antimony, can be substituted in occasional lattice positions in place of the germanium or slicon atoms, and since they require only four of their electrons to form the four covalent bonds, the extra electron becomes an excess electron, thus creating an excess semiconductor.

On the other hand, replacement of some of the atoms in germanium or silicon by atoms with three outer electrons, such as boron, aluminum, gallium, or indium, brings about a deficiency of electrons and, therefore, a deficit semiconductor. In some very interesting experiments (Scaff, Theuerer, and Schumacher, 1946), a melt of silicon containing both boron and phosphorus was cooled very slowly, with the result that the first part of the silicon ingot to solidify contained more boron impurity, while the inside contained more phosphorus with a transition from one to the other in between. The result was that the first part was a *p*-type or deficit semiconductor and the last part was an *n*-type semiconductor. In between the two regions, there was a fairly small region where the two effects cancel each other resulting in a high resistance. Such *p*-*n* junctions are equivalent to the barrier layers and have rectifying and photovoltaic properties.

These ideas of semiconductors and solids, in general, have been very useful in the understanding and development of such diverse things as: radar detectors, transistors, alternating current rectifiers, thermistors, photocells, phosphors, metal oxidation theories, etc.

THE METAL TO SEMICONDUCTOR CONTACT

In many of the applications of semiconductors, a metal to semiconductor contact is involved. Further, Schottky showed that for rectifiers and photovoltaic cells this contact must also involve a "barrier layer," which in effect acts as a (variable) high resistance layer. This layer may be a "chemical" barrier, consisting of a very pure semiconductor as in cuprous oxide cells; another compound as in selenium cells; a "physical" barrier, such as a layer of varnish; or a "natural" barrier, inherent in metal to semiconductor contacts.

In a metal, the electrons occupy, to a very large extent, the lowest energy levels possible in a manner dictated by the Pauli principle. The top level occupied at a temperature of absolute zero is called the Fermi level. At any other temperature a few of the electrons from the topmost levels are excited thermally, and the dis-

tribution of the electrons follows the Fermi-Dirac statistics. The amount of energy required to remove an electron from the Fermi level into free space is called the work function is represented by W_m in figure 3A.

In an excess semiconductor, as shown in figure 3A, there are a few electrons in the conduction band, being contributed by the donor atoms in the bulk semiconductor. The work function, W_s, represents the energy required to lift the electron from the bottom of the conduction band into free space. Even at ordinary

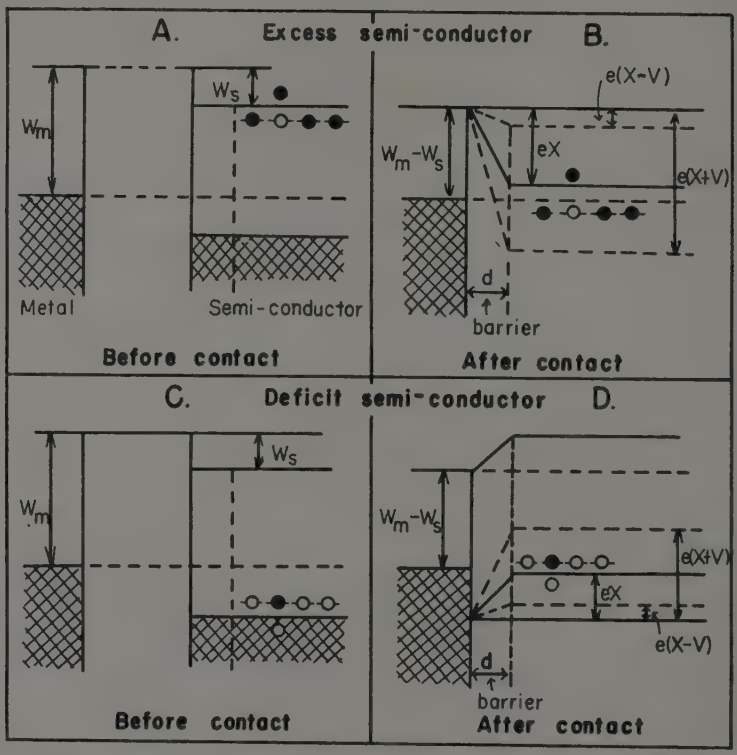


FIGURE 3. The energy level diagrams for metal to semi-conductor contacts with chemical barriers at the interface. The changed barrier heights which are due to externally applied voltages and which are responsible for rectification are shown by the indicated dashed lines.

temperatures, a very small number of electrons can acquire the necessary energy to overcome the work function and escape, both in the case of the metal and of the semiconductor.

When the metal is brought in contact with an excess semiconductor, a situation initially like figure 3A results, where the work function for electrons in the metal to escape to the semiconductor is the difference W_m-W_s. The chemical potential or the number of electrons escaping from the metal is less than from the semiconductor, because of the larger energy requirement, so that there is initially a net electron flow to the metal. This flow results in charging the metal negatively

and the semiconductor positively, thus raising the energy levels of the metal relative to those of the semiconductor. The process continues until equilibrium is attained when the electron flow in one direction is balanced by the flow in the other direction. Equilibrium is reached when the Fermi level of the metal is about midway between donor levels and the bottom of the conduction band of the semiconductor, as shown in figure 3B. The bottom of the conduction band of the semiconductor is depressed by an amount X on a potential scale, so that the amount of energy required to lift an electron over the barrier is eX. The barrier, of course, remains as shown, its width being represented by d.

The case of the contact of a metal to a p-type semiconductor is more involved. In the semiconductor, some of the electrons are bound by the acceptor atoms, so that positive holes exist in the previously filled band, as exemplified by cuprous oxide and selenium. In such deficit semiconductors, the positive holes may be regarded as the conductors instead of electrons, as in the excess semiconductors. The energy level diagrams for a metal and such a semiconductor is shown in figure 3C. In cases of interest, the electrons are initially at lower energy in the semiconductor than in the metal, so that when contact is established between the two, a transfer of electrons from the metal to the semiconductor results. One may regard the transfer of electrons to occur to some of the acceptor atoms in the semiconductor or alternatively regard the electrons as cancelling some of the positive holes in the semiconductor. In any case, the result is that the semiconductor becomes negatively charged with respect to the metal, thus raising the electron levels of the semiconductor relative to the metal to such an extent that the Fermi level in the metal falls about half-way between the filled band and the acceptor levels, as shown in figure 3D. A barrier height of eX in energy, is created.

MECHANISM OF RECTIFICATION

The Mott-Schottky picture described above was devised particularly to explain the mechanism of rectification of electric current, and it succeeds quite well in this. If an excess semiconductor in contact with a metal is made negative, with the respect to the metal, by a voltage V from an external source, the energy levels of the electrons in the semiconductor are raised by an amount eV, as shown in figure 3B. The equilibrium is upset, so that a net transfer of electrons from the semiconductor to the metal results. Another way of viewing the situation is that the barrier is reduced to X-V by the negative voltage on the semiconductor. The direction of easy electron flow is called the forward direction for the rectifier. For the reverse direction when the metal is negative with respect to the semiconductor, the barrier is increased to $X + V$ thus setting up a high resistance for electron flow.

For the case of the deficit semiconductor in contact with a metal, a negative potential on the semiconductor increases the barrier height to $X + V$, as in figure 3D, so that this is the high resistance direction. Making the metal negative decreases the barrier to $X - V$, so that the direction of easy electron flow is from the metal to the semiconductor as shown. This is the situation for selenium and cuprous oxide semiconductors.

A more unified point of view of both types of semiconductor rectifiers would be to consider that a negative potential on the excess semiconductor is required to hasten the current carriers (the electrons) toward the metal. For the deficit semiconductor, a positive potential on the semiconductor drives the current carriers (the positive holes) toward the metal.

The discussion here has been limited to chemical barrier layers, but equally satisfactory explanations have been made for other types of barriers. Also, this discussion has treated the barrier as one of constant width and variable height and has implied movement of the conductors over the barrier. Other treatments consider the variation of the width of the barrier, say with applied potential, and

the penetration of the barrier by conductors by tunnelling mechanism. Another phenomenon that should be mentioned here is that the junction between a *p*-type and an *n*-type semiconductor constitutes a barrier with rectifying and photovoltaic properties (Scaff, Theruerer, and Schumacher,1946). (In transistors, where amplifying properties are desired, such that a small signal at a junction can control a large current across the junction, a further refinement involves a sandwich of a *p*-type semiconductor between two zones of an *n*-type semiconductor, creating a so-called *n-p-n* junction. The double barrier created constitutes a potential "hook" which is sensitive to small potentials applied on the p-type slab relative to one of the *n*-type slabs. This controls a large current from the *n* slab to the other *n* slab across the junction).

Another variation of the barrier layer theory is the theory of surface states due to Bardeen (1947). The surface of a semiconductor cannot have exactly the same electronic structure as the bulk of the semiconductor. If new energy levels exist at the surface which are in the forbidden zone of the bulk semiconductor, the surface may act as a metal with respect to the interior. By this view, a rectifying barrier is inherent within the surface of a semiconductor, so that in metal-semiconductor rectifiers, the metal serves as merely a contact instead of creating the natural barrier. This theory successfully explains the previously puzzling fact that the properties of rectifiers are not usually dependent on the work function of the metal used. However, in the interests of simplification, these various ramifications of the barrier layer theory are not being further detailed here.

MECHANISM OF THE PHOTOVOLTAIC EFFECT

The photovoltaic effect may be explained as an extension of the rectifier theories and in fact the theories of Schottky and Mott were originally devised for the purpose of explaining both effects.

If one considers a deficit semiconductor, such as cuprous oxide, the establishment of a contact between the semiconductor and a metal approximates initially the condition of figure 3C. Because of the difference in the energy levels of the electrons in the metal and the semiconductor, electrons are preferentially transferred from the metal to the nearest acceptor atoms in the semiconductor, which results in charging the semiconductor negatively with respect to the metal, and conversely the metal positively with respect to the semiconductor. The process continues until the rates of transfer of electrons in both directions are the same. This equilibrium situation is reached when the Fermi level of the metal is about half-way between the filled band and the acceptor levels, as shown in figure 3D. Thus, the equilibrium condition is one in which the semiconductor is negative with respect to the metal.

For the purpose of explaining the photovoltaic effect, the mechanism becomes somewhat clearer if a "natural" barrier layer is postulated, in which the metal is in contact with a semiconductor of the same composition as the bulk of the semiconductor, so that the barrier is inherent in the contact. The character of semiconductor in contact with the metal in the case of selenium or of cuprous oxide is not known with any certainty, but it is still widely held, as in early theory, that chemical barriers are present. A third alternative arises based on Bardeen's theory of surface states, but it is believed by some not to apply to selenium or to cuprous oxide.

Figure 4 sketches the situation of the contact between a metal and a deficit semiconductor, with a natural barrier. As described before, electrons are transferred from the metal to the nearest acceptor atoms in the semiconductor, making the semiconductor negative with respect to the metal. This picture differs from figure 3D in that here a gradient of filled acceptor levels exists in the barrier layer.

When a semiconductor is illuminated, the energy, $h\nu$, of the light quanta may be absorbed and used to excite electrons from lower levels to higher levels. For

such frequencies of light that the energy of the quanta is sufficient to lift electrons from the filled band to the acceptor levels, a large improvement in conductance during the illumination is obtained, because of the positive holes created. This improvement is called photoconductance. In the bulk of a semiconductor, light of sufficiently higher frequency or shorter wave length can excite electrons from the filled to the unfilled band of the semiconductor, as shown in figure 4. These electrons fall very quickly to empty acceptor levels and some eventually fall to the (nearly) filled band to cancel some of the positive holes.

In a photovoltaic cell in which the semiconductor is in contact with a metal, the acceptor levels in the semiconductor near the metal are already filled due to the charging process required for the attainment of equilibrium. Here, the photo-excited electrons in the vicinity of the barrier cannot fall into acceptor levels so that their life-time in the excited state is longer than those in the bulk semicon-

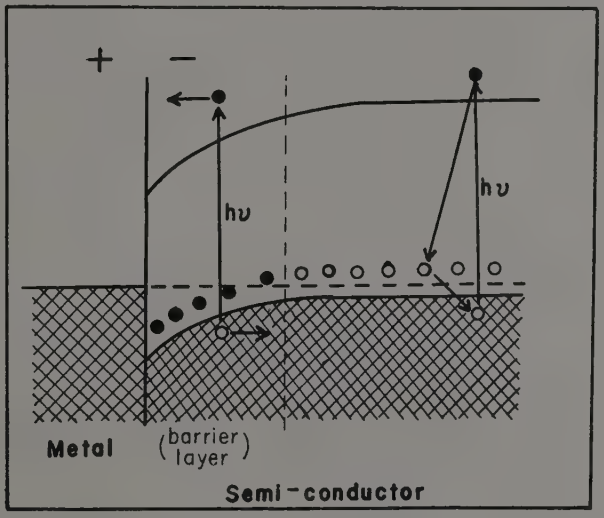


FIGURE 4. The mechanism of the photovoltaic effect. The contact of a metal to a deficit semi-conductor with a natural barrier is shown.

ductor. Because of the space charge which exists at the barrier with the semiconductor negative with respect to the metal, the excited electrons in the conduction band are driven toward the metal. If the circuit is completed externally, the electron current toward the metal is accompanied by a migration of positive holes in the opposite direction, since, of course, the positive holes cannot continue to accumulate in the semiconductor. For an open circuit and high levels of illumination, initially the photoelectrons arriving at the metal will reduce the positive charge on the metal and thus diminish the barrier. This will, in turn, cause a drift of positive holes toward the metal and the steady state, at which the numbers of electrons and positive holes arriving at the metal are equal, will be characterized by a certain open circuit photopotential. The open circuit potential will approach the magnitude of the original barrier, since the net drift of photoelectrons will continue as long as any appreciable amount of the original charging potential remains.

PHYSICAL PROPERTIES OF PHOTOVOLTAIC CELLS

The most important property of a photovoltaic cell is its self-generation of current which makes it independent of external sources of potential.

The spectral sensitivity of the cuprous oxide and selenium photocells lies in and near the visible portion of the spectrum, as shown in figure 5. The selenium cell responds from about 3000Å. to above 7000Å. with a maximum response at 5700Å. The front-wall cuprous oxide cell yields a photoelectric current from about 3000Å. to 6000Å. with a maximum at about 5000Å. The back-wall cuprous oxide cell responds from about 6000Å. and continues into the infrared. It is insensitive to wave lengths shorter than 6000Å. because this light is absorbed in the bulk cuprous oxide, so that it does not reach the photosensitive surface. All of the curves represented give relative response for constant light energy with the

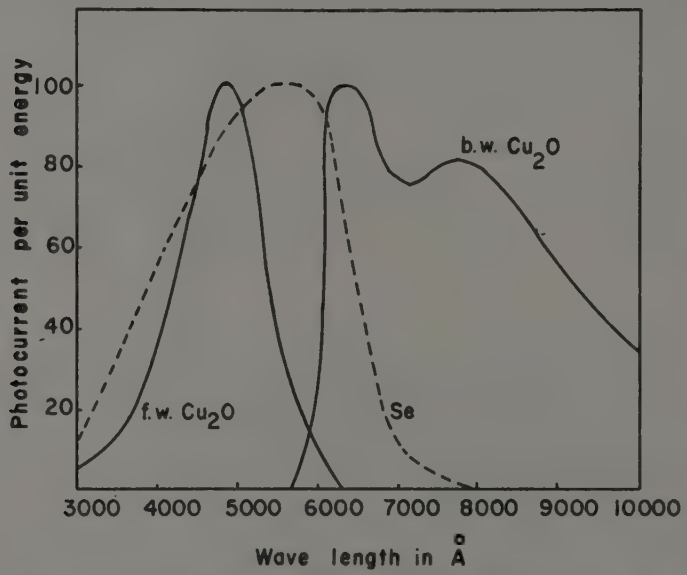


FIGURE 5. The spectral sensitivities of photovoltaic cells of the selenium and front-wall and back-wall cuprous oxide types.

maximum in each case taken arbitrarily as 100. The curves are typical, but the exact values will vary slightly from cell to cell, depending on the manner of preparation and on the light transmission of any substances interposed between the light and the photosensitive surface, such as cover glasses or semitransparent metal films.

The photocurrent depends upon light intensity, but the dependence is affected by other variables. An equivalent circuit is given in figure 6A, where I is the primary photocurrent, C is an internal shunting capacitance, R_i is an internal shunting resistance, R_s is a series resistance, R_c is an external contact resistance, and R_L is an external load resistance. The series resistance, R_s, is due to the bulk semiconductor, and R_c is due to the top electrode (the sum of the two being about 50 ohms for a typical 2-inch selenium cell). The internal resistance, R_i, is due to the barrier and this varies according to conditions, in this case of external resistance and light intensity, as shown by curves *a* and *b* in figure 6B. Typical values for R_i are of the order of several hundred to several thousand ohms.

The open circuit potential varies with light intensity approaching a saturation value of about 0.3 volt at high intensities for a typical selenium cell. In addition

to light intensity, the external photocurrent for any given cell depends also upon the external resistance, as is seen by comparing curves c^* and d^* in figure 6B. For very low external resistance, the photocurrent varies linearly with light intensity up to quite large levels of illumination. For increasing values of external resistance, the photocurrent departs from linearity at lower and lower levels of illumination. In terms of the equivalent circuit, the photocurrent in the external resistance is given by: $I_{ext} = IR_i/(R_i + R_L + R_c + R_s)$, with the caution, of course, that R_i is not constant. For measurements with very low external resistances of the order of a few ohms, the slope of linear curve c^* is about 500 microamperes per lumen for a typical cell of about 10cm² area.

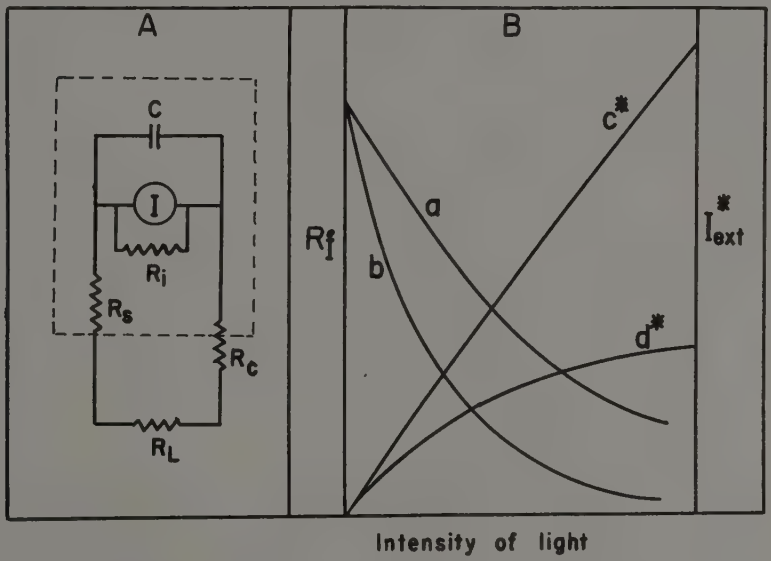


FIGURE 6. A. The equivalent circuit for a photovoltaic cell. The dotted rectangle encloses the circuit elements belonging to the cell proper. B. The dependence of the internal resistance and the photocurrent (*) on light intensity. For a and c*, a low external resistance was used, and for b and d*, a high external resistance was used.

The power output is given by the product of the load resistance by the square of the output current (i.e. $R_L I^2_{ext}$) and this would be a maximum when the external resistance is equal to the internal resistance, if the internal resistance were constant. However, since the internal resistance is not constant, the optimum external resistance varies according to the intensity of illumination.

Temperature also has an effect on current output, but for the present purpose, it is sufficient to state that this variation is in most cases not more than 10 percent for about a 20° C variation in the vicinity of room temperature. The stability of photovoltaic cells is a chemical and mechanical problem, in that corrosion and such factors determine deterioration. There is no inherent reason for deterioration (electrolysis does not accompany conduction) and, in fact, well-sealed cells have a very long life.

One important factor which arises in the prolonged use of photovoltaic cells is the problem of fatigue. Discounting the external deterioration effects, most of the fatigue appears to be reversible such that the cell recovers after a short rest.

Lange (1938) found that a short-circuited selenium cell exposed to sunlight for 50 days decreased in output by less than 10 percent, with the measurements themselves made under moderate intensities. Measurement of the output under high light intensities shows a relatively quick attainment of a constant output, the time required being of the order of a few minutes.

Another property of photovoltaic cells which is important for certain situations, is that they exhibit an electrical capacitance. However, this is of importance only when the light fluctuations are very rapid, of the order of several thousands per second.

CONVERSION OF SOLAR ENERGY INTO ELECTRICAL ENERGY

The consideration of the possibility of conversion of solar energy into electrical energy must begin with a discussion of efficiency. Zworykin and Ramberg (1949) calculate an efficiency of 0.5 percent, using the power output of a selenium cell as 50 microwatts per lumen and the light content of solar radiation as 100 lumens per watt. Direct experimental measurements by Telkes on a cell of 10 cm^2 area receiving illumination of 0.7 watts gave 1.8 milliamperes output at a load voltage of 0.12 volts for an efficiency of 0.03 percent. Preston (1950), with a selenium cell coated with CdO, obtained 0.7 milliamperes per lumen and an open circuit potential of 0.5 volts, which recalling that the load voltage is about half of the open circuit voltage, calculates to an efficiency of over 1 percent. Kosenko and Miselyuk (1948) found silver sulfide cells to be effective from 4000 Å. to 14,000 Å., yielding usually 4 ma. per lumen and sometimes as much as 8 ma. per lumen, with potentials of 0.15 volts. On the other hand, Houstoun (1948) tested several commercial cells, probably selenium, with very much less optimistic results.

There appears to be no obvious theoretical limitation on the efficiency of conversion of solar energy in electrical energy by photovoltaic cells, for example, of the sort that thermodynamics dictates in the case of heat engines. The low efficiencies quoted above represent the present state of development in a field in which no great effort is being made to improve the efficiency of power conversion. In the following calculations an efficiency of 0.5 percent will be used as representing a good present possibility. When a substantial improvement in efficiency is attained, the required photocell area can be reduced proportionately.

Using the average figure for solar radiation, given by Dr. Shaw in this series, of 1000 hp per acre over a 24-hour period, one can calculate a total energy of 3.7 kw-hr per day per square yard. At an efficiency of 0.5 percent, the yield of electrical energy is 0.019 kw-hr per day per square yard. The average domestic consumption of electricity per householder is 5 kw-hr per day, as calculated from data given by Ayres and Scarlott (1952). This means that the average household would require an area of 260 square yards, which would be a plot of 30 ft X 80 ft (roughly the area of a roof on a ranch type home). In winter, where Shaw's figure of 420 hp applies, roughly twice as much area would be needed and in more favorable latitudes and seasons, less area would be required. Of course, since the time of day that electricity is used is not the same as the time when sunlight is available, a storage of energy is implied.

The total consumption of electricity in the United States, for all purposes, is over 300 x 10^9 kw-hr per year or about a billion kw-hr per day and the installed capacity is about 80 million kilowatts, with both rising rapidly. The present capacity could be furnished at the photovoltaic cell efficiency of 0.5 percent by an area of 30,000 square miles, which is a circular area of about 100 miles radius roughly one-third of the area of any one of the states, Arizona, New Mexico, or Nevada.

The calculations given here are based on present efficiencies. At present, the capital costs of any such installations would probably be prohibitively high compared to present methods of power generation, except for certain isolated

areas or special uses. However, the design of the cells is quite simple and it is easy to envision cheap, large-scale methods for their manufacture, for example, by a continuous strip rolling and coating process. Another minor disadvantage is that current from photovoltaic cells is direct current and the cells are most efficient on a limited load. However, these are not real disadvantages, since motors could be wound for maximum efficiency, and the motors could be used to drive alternating current generators so that the voltage could be stepped up for long line transmission.

Still other problems are details requiring engineering solution. The fatigue at high light intensities could be minimized by using acute angles of incidence for the light. Also, since particular photovoltaic cells have limited spectral sensitivities, a combination of types of cells could be used (e.g., selenium and back-wall cuprous oxide cells complement each other nicely, giving response throughout the visible and a considerable portion of the infrared). Here some sort of non-subtractive light dispersion device would be required. Because of the independent time variation of sunlight intensity, so that production cannot be sensitively tailored to demand, new or re-examined old concepts of electrical energy storage would have to be developed. For example, water could be pumped up-hill during the day and then used to generate power at night, or a chemical product could be made by electrolysis for later use in energy release.

Much of the previous discussion is based on the energy conversion efficiency of 0.5 percent. The obvious starting point for any practical consideration of conversion of solar energy is to improve this efficiency radically. A ten-fold increase of efficiency to 5 percent, a quite reasonable expectation, would mean a ten-fold decrease in the area requirement. As pointed out before, there appears to be no theoretical limit on the efficiency. Past applied research has been concerned more with improvement of stability rather than of efficiency. In view of the large amount of fundamental information clarifying our ideas on semiconductors which has recently been obtained in radar and transistor research, the time is now ripe for research to make substantial advances in the field of photovoltaic cells.

It should be mentioned that another method of converting solar energy into electrical energy is by means of the thermoelectric effect. The principle of the method is as follows: if a junction of two dissimilar materials is maintained at a higher temperature than another similar junction, a potential difference will be set up between the two junctions and a current will flow in a circuit. For solar energy conversion, sunlight would be absorbed, converted to heat, and used to heat the hot junction. A device using this method would be essentially a heat engine and its maximum theoretical efficiency would be limited, as pointed out by Shaw, by the two operating temperatures, as given by thermodynamics. The actual efficiency is a cumulative result of the several parts of the process (efficiency of absorption of light and conversion to heat, reduction in heat losses, etc.) as well as the thermoelectric efficiency itself. The thermoelectric efficiency has been considered by Telkes (1947) and she found experimental efficiencies up to 7 percent with a 400° C. temperature difference, using junctions of lead sulfide with an antimony-zinc alloy. For direct measurements of solar energy conversion, Telkes found about 1 percent efficiency for a flat plate type of generator with a temperature difference of 50–70° C. and she forsees a probable maximum of 2 percent. With additional light concentration devices, such as mirrors and lenses, to raise the temperature difference to 300–400° C., she obtained efficiencies of up to 3.5 percent.

It is difficult to compare the practical potentialities of the various possible methods of using solar energy since in each of them the room for possible improvement is large and the efficiency requirement for feasible operation is fairly small.

The thermoelectric generator, like all heat engines, suffers from the disadvantages of a theoretical limit on efficiency and the necessity of concentrating the light. Its efficiency in conversion of heat into power does not yet compare with vapor heat engines, but this is due probably to the lack of sufficient development. Certainly the thermoelectric effect deserves further investigation as a possible means of solar energy conversion.

REFERENCES

Ayres, E., and **C. A. Scarlott.** 1952. Energy sources. McGraw-Hill Book Co., New York.
Bardeen, J. 1947. Surface states and rectification at a metal semiconductor contact. Phys. Rev. 71: 717–727.
Copeland, A. W., O. D. Black, and **A. B. Garrett.** 1942. The photovoltaic effect. Chem. Rev. 31: 177–226.
Henisch, H. K. 1949. Metal rectifiers. Oxford University Press, London.
Houstoun, R. A. 1948. The efficiency of the barrier layer photocell. Phil. Mag. 39: 902–910.
Kosenko, V. E., and **E. G. Miselyuk.** 1948. Physical characteristics of silver sulfide photocells. Zhur. Tekh. Fiz. 18: 1369–1377.
Lange, B. 1938. Photoelements. Reinhold Publishing Corp., New York.
Lehovec, K. 1948. The photovoltaic effect. Phys. Rev. 74: 463–471.
Mott, N. F., and **R. W. Gurney.** 1948. Electronic processes in ionic crystals. Oxford University Press, London.
Ohl, R. S. U. S. Patent 2,402,662 (June 25, 1946).
Pfann, W. G., and **J. H. Scaff.** 1949. Microstructures of silicon ingots. Jour. Metals 1: 389–392.
Preston, J. S. 1950. Constitution and mechanism of the selenium rectifier photocell. Proc. Roy. Soc. (London). A202: 449–466.
Scaff, J. H., H. C. Theuerer, and **E. E. Schumacher.** 1949. P-type and n-type silicon and the formation of the photovoltaic barrier in silicon ingots. Jour. Metals, 1: 383–388.
Schottky, W. 1942. Simplified and extended theory of barrier-layer rectifiers. Z. Physik. 118: 539–592.
Seitz, F. 1940. Modern theory of solids. McGraw-Hill Book Co., New York.
———. 1943. Physics of Metals. McGraw-Hill Book Co., New York.
Shockley, W. 1950. Electrons and holes in semiconductors. D. Van Nostrand Co., New York.
Telkes, M. 1947. The efficiency of thermoelectric generators. I. Jour. App. Phys. 18: 1116–1127.
———. 1951. Future uses of solar energy. Bull. Atomic Scientists, VII, 8: 217–219.
———. Private communications.
Torrey, H. C., and **C. A. Whitmer.** 1948. Crystal rectifiers. (MIT Radiation Laboratory Series.) McGraw-Hill Cook Co., New York.
Williams, A. L., and **L. E. Thompson.** 1941. Metal rectifiers. Jour. Inst. Elec. Eng. (London). 88: 353–371.
Wilson, A. H. 1939. Semiconductors and metals. Cambridge University Press.
Zworykin, V. K., and **E. G. Ramberg.** 1949. Photoelectricity. John Wiley & Sons, New York.

THE USE OF OPTICAL SYSTEMS IN THE UTILIZATION OF SOLAR ENERGY

J. ALLEN HYNEK

Director, McMillin Observatory, The Ohio State University, Columbus 10

Sunlight falls on the earth as a nearly parallel rain of photons, distributed in energy reasonably in accord with a Planck curve of 5700° K. The atmospheric blanket of the earth, however, exacts an appreciable toll of this photonic energy in the ultraviolet and in the infrared, but fortunately transmits all but about one-sixth of the energy in the richest part of the solar spectrum—the visible.

As in the case of ordinary rain, which can be used as it falls to promote the growth of crops or as a concentrated torrent to operate turbines, so can the rain of

sunlight be used as it falls, or in mildy concentrated form, for certain purposes of energy transformation; and in a highly concentrated form for other purposes, notably those for which high temperatures are essential. In short, the transformation of solar to other forms of energy, depending on the particular method, can be characterized by the temperature differential at which the energy transformation is most efficiently effected. This temperature differential can vary from nearly zero in the case in which the energy transformation occurs say, by the drying out of chemical salts or the growth of *Chlorella* to those temperatures at which virtually all known substances vaporize. The laws of thermodynamics state that the maximum amount of work that can be obtained from the transformation of thermal to other forms of energy is given by the temperature drop in the process divided by the final temperature ($\Delta T/T$). This means that most schemes for the utilization of solar energy are grossly inefficient because they operate with small temperature differentials.

If the temperature differential for a given process is specified, this in turn specifies, within a relatively narrow range, the kind of optical system needed. That is to say, if our objective is simply to heat water for low grade energy transport, a quite different optical system will be called for from one whose purpose it is to produce high temperatures necessary to melt refractory substances.

Whichever optical system is used, however, it must conform to certain elementary optical principles. The kind of practical results these principles allow and the kind of limitations they impose on the physical structure of optical systems for these purposes follows directly from their application. These results and limitations may come as a surprise to many who have not had the occasion to think about these matters. And, of course, no matter how elaborate and fanciful the mirror-and-lens systems are made for the utilization of solar energy, these elementary optical principles cannot be circumvented.

We can start with perhaps the most basic of all physical principles—the second law of thermodynamics—which states, in effect, that no selfsustaining method can be devised for transferring heat from a cooler to a hotter body. This means, in our context, that no optical system whatever will enable us to produce higher temperatures than 5700° K—the surface temperature of the sun. To the uninitiated, it might appear that if a large enough collecting surface were used, enough sunlight might be collected and concentrated to produce a hot pit of incredibly high temperature. This, unfortunately, the second law of thermodynamics will not allow, but temperatures higher than any ordinarily sustained on earth can be produced as long as the sun shines. Furthermore, temperatures as high as 3000° and 4000° K. can be produced which give a pure uncontaminated heat, free of chemical byproducts which are present almost of necessity when the high temperatures are chemically or electrically produced. The production of such high temperatures in this pure form is particularly valuable when one wishes to study the behavior of substances at high temperatures without bringing these substances into contact with any others. Indeed, the rays of the sun can be directed into a vacuum chamber in which only the object to be treated is present. It is interesting to note that a black body heated to maximum temperature by sunlight in this manner will emit far more ultraviolet light than contained in sunlight at the surface of the earth.

The production of high temperatures is, however, a very special application and, in general, solar light need not be highly concentrated in order to do useful work. Since the limitations imposed by optical principles, however, apply to all cases, we proceed directly with their discussion.

Any optical system can be characterized by its effective aperture and its effective focal length, and by the ratio of these two. We say "effective" because in certain cases the optical system is no longer simple, that is, one in which the aperture is simply the physical opening of the system and the focal length the simple distance

from the lens or mirror surface to the focal or image plane. Actually, when one looks at the matter more closely, one sees that we are not primarily dealing with image formation at all but rather with the position of the minimum cross section of the total bundle of rays. That this is not the same thing as the place of image formation can be seen by the simple experiment of projecting the image of the sun with a typical telescopic system. This is done by holding a sheet of paper several feet in back of the eyepiece of a telescope. By adjusting the eyepiece slightly, a large sharp image of the sun is obtained on the paper, of sufficiently good definition to show sunspots and even solar granulation. As one moves the sheet of paper toward the telescope, however, the image becomes indistinct and finally thoroughly blurred, but as the paper is moved still closer to the eyepiece it bursts into flame. The greatest concentration of energy does not, therefore, correspond necessarily to the place of image formation.

Rather, it might be put this way: the aim of optical systems for the utilization of solar energy is the production of a usable concentration of solar rays, not of a solar image suitable for photography. Thus, a rough spherical mirror of long focal length used with a mirror or lens of short focal length can be constructed at a very small fraction of the cost of a telescopic optical system, and yet can be made to produce a concentration of light for energy purposes that will essentially equal that of the more expensive telescopic system.

In this short treatment, it would carry us too far afield to examine anything but the simpler optical systems. In these the aperture can be defined as the total light-gathering area and the focal length can be defined in the usual way. Using the word "image" rather loosely, the size of the image will depend, of course, only on the focal length. A handy "thumb rule" for the size of the sun's image, for any optical system, is to divide the focal length by one hundred and eleven (f/111). A reading glass of, say, six inches aperture and a focal length of one foot will give an image of the sun about a tenth of an inch in diameter; a telescope typical of those used on college campuses, having a focal length of, say, 175 inches, will yield an image of the sun about an inch and a half in diameter. The great Yerkes refractor of focal length 63 ft. gives an image of the sun that is nearly 7 in. in diameter, and, if the large reflector of the Perkins Observatory, of focal length 104 ft. were used on the sun (which, of course, it never is) we should have an image at the Cassegrain focus of nearly a foot in diameter.

One is reminded of the war-scare stories of the Germans' intention to launch an artificial satellite some hundreds of miles in space equipped with a lens or mirror system to focus the sun's rays and thereby wipe out entire cities. We need have little fear of this since the size of the sun's image would increase in diameter by approximately one mile for every one hundred or so miles the lens was farther out in space. It would take a huge mirror to collect enough light so that, when spread over an area of many square miles, the energy density would be sufficient to vaporize cities. However, it would still be possible for an enemy with an artificial satellite-lens of imaginable proportions to raise the temperature in a city sufficiently to make living in that city very uncomfortable.

Elementary calculation shows that a mile-diameter mirror or lens at 222 miles above the earth's surface would yield an "image" of the sun having approximately four times the area of the light gatherer. Even if occultation effects were absent, the sunlight on the target area would be increased by one-fourth its normal value. Applying simple black-body considerations, the momentary increase in temperature amounts to not more than 30°F. We say "momentary" since the optical system would be in rapid revolution about the earth, completing a round trip in about two hours.

The aperture of a lens system determines the total amount of energy that can be gathered. The focal length determines over how wide an area this energy is distributed. Consequently, the f/number, or the ratio of the focal length to the

aperture, alone determines the energy density in the image. If one assumes black body conditions for the receiver, the temperature of the receiver can be determined from Stefan's law, and is likewise solely a function of the f/number. A small hand magnifier is thus capable of concentrating as much solar energy per unit area as a large telescope of the same f/number, if the optical excellence of the two systems is the same. As an example, let us take the world's largest refracting telescope—the Yerkes refractor—and a reading glass 4 in. in diameter and of 8 in. focal length. The Yerkes refractor has an objective 40 in. in diameter and a focal length of 63 ft. The telescope gathers, therefore, 100 times as much flux as the reading glass but spreads it into an area that is nearly 9,000 times as great as the area covered by the image formed by the reading class. Its ability to produce heat-at-a-point is, therefore, some 90 times less than that of a simple reading glass. The reading glass, however, gives a solar image less than 0.1 in. in diameter while the Yerkes refractor produces an image nearly 7 in. in diameter.

As a further example, take the world's largest telescope, the 200-inch reflector at Palomar. A precise reflector of this kind is never directed toward the sun because of the distortion of the figure that would result by this procedure. Nonetheless, if it were used on the sun, all the sunlight falling on the mirror area of more than 200,000 sq. cm. would be concentrated in an image 177 sq. cm. in area. Now, although the solar constant is generally stated as 1.94 cal./min./sq. cm., this refers to energy received outside the earth's atmosphere. Measures made at Mt. Wilson with the sun near the zenith show that only 1.54 cal./min./sq. cm. are received, representing a loss of about one-fifth of the total. Thus the total energy received by the 200-inch telescope would be 2.18×10^{11} ergs/sec. Assuming no losses in the optical system, the image receives 1.23 x 10 ergs/cm. which, under black body conditions, corresponds to a temperature of 2,150° K. The 200-inch telescope has a focal length of 660 in. and therefore an f/number of 3.3. A similar calculation carried out for a 6-inch aperture, 12-inch focal length reading glass shows that although the image has an area of but 0.06 sq. cm. the image receives energy at the rate of 3.26 x10 ergs/sec./sq. cm. The black body temperature is therefore 2,750° K.—some 600° higher than that given by the world's largest telescope.

These illustrations are, of course, simple and do not take into consideration the temperature of the surroundings, the conduction of heat away from the receiver, and other factors. They serve merely to illustrate that while large telescopes collect a great deal of energy, it is less concentrated than in the case of a simple hand magnifier.

It is amusing to consider what would happen if the 6-inch image given by the world's largest telescope were further concentrated by the simple reading glass of 6-inch aperture and focal length of 12 in. If the full 6-inch image were allowed to fall directly on this reading glass, a concentration of energy would occur in an area 3.7 in. in diameter, slightly more than one foot beyond the normal focal plane of the 200-inch telescope. The energy density would be increased by a factor of 2.6 and the black body temperature to 2,730° K. so that the temperatures are essentially equal; the area of the image has been increased from 0.1 in. to 3.7 in. and thus far more energy is available for work at that higher temperature. The fact that the secondary lens would become quite warm is merely a practical difficulty and does not destroy the value of the illustration.

Now let us consider briefly the relative merits of paraboloidal and spherical mirror systems. We are accustomed to thinking of a parabolic surface as the ideal light gathering medium. The formula for a parabola, $y^2 = 4fx$, where f is the focal length of the parabola, indicates that simply by constructing increasingly "cigar-shaped" light collectors, very small f/numbers and thus extremely high temperatures could be obtained. One needs here, however, to reckon with the fact that the sun is not a point source. Conn (1951) has recently described a

parabolic receiver of aperture 120 in. and a focal length of 34 in. This implies an f/number of 0.3. If one traces rays for the system one finds, however, that the image size corresponds to a focal length of 7 ft. and hence an f/number of 0.7. This is merely to illustrate that short focus parabolas are extremely sensitive to off-axis rays, and even the half degree subtended by the sun produces a notable distortion. Preliminary calculations indicate that it would be better, and probably cheaper, to construct a large-aperture spherical mirror of say, f/20 ratio in which, therefore, the spherical aberration is not serious, and to further collect and concentrate the beam by a small auxiliary lens or mirror on to the receiver. The secondary mirror would, of course, have to be constructed of a highly refractory substance.

If we get away from high energy densities and speak rather of high total energies at lower densities, we are much more likely to be dealing with examples which will be useful. Let us suppose a hypothetical example of this sort, an industrial plant located in an open, semi-arid region, or at least in a region having cheap land nearby. A black hemisphere to act as an energy collector is mounted atop a tall tower, giving the appearance of a tall water-storage tank. At the base and extending out for several acres we shall have an array of plane mirrors, or perhaps slightly spherical mirrors of very long focal length. These shall be directed to deflect the sun's rays to the black receiver atop the tower. Modest power needs could be supplied by such an arrangement at a relatively small cost.

Let us imagine, however, a solar installation on a much larger scale. Since we are not limited in our imagination, let us choose a valley surrounded by a ring of mountains. If the valley had a radius of one mile, 10,000 plane mirrors, each of one square yard area mounted so as to form the elements of a large spherical reflector would produce, applying the simple rule-of-thumb, an image of the sun, a mile away, some fifty feet in diameter. If a 50-foot diameter black sphere were placed in the center of the valley, simple calculation shows, even making generous allowance for losses in transmission and general inefficiency of the system, that more than one hundred gallons of water could be brought to boil per minute and more than ten gallons could be converted into steam per minute. Even so, 10,000 mirrors would cover but a few acres and if much larger parts of the mountain-ringed valleys were employed, enough solar energy could be transformed to supply a good-sized community with power. One needs only to remember that each mirror receives the equivalent of better than one horsepower and that even a small-sized valley could accomodate several million mirrors. Even allowing for 10 percent efficiency of the entire system, it can be seen that a solar energy project on this scale would develop many hundreds of thousands of horsepower for industrial purposes. If power were not the object but instead merely the heating of great quantities of water to, say 150° F, a large community could be heated by a relatively modest solar energy plant. The entire storage system, of course, would have to have sufficient heat capacity to act as a reserve for cloudy periods.

Numerous schemes for low temperature solar engines have been proposed from time to time (Conference on the Sun in the Service of Man, 1951) and some small installations are now in operation.

As far-fetched as some of these optical schemes may seem, it seems clear that eventually solar energy must be used more directly for human needs. The astronomical time-scale for the earth is rated in the billions of years; and if present theories of the source of solar energy are correct, the climate of the earth will not change sensibly for the next 10,000,000,000 years. In this period nature would have time to start the entire process of evolution from amoeba to man several times over, should man destroy himself and other forms of life. Ordinary natural resources will most probably be exhausted long, long before this. Over long periods of time, atomic energy likewise is not the final solution since it, itself, permanently destroys supplies of the critical heavier elements. The only apparent eventual answer seems to be the use of solar energy.

The eventual answer must also make better use of the high energy potential (low entropy) of solar photons, characteristic of radiation at 6,000°C, rather than of their utilization after degradation to thermal motion by black body absorption—that is, advantage should be taken of the "ability to do work" of the individual photon, rather than to attempt to put solar energy to work after the entropy of the system has been increased and the same total energy reduced to a less useful form. In both types of usage, however, the optical principles enumerated above must be obeyed.

In the words of the advertiser, "Eventually, why not now?": Experiments on a sufficiently large scale might well be made now so that the human race might gain some experience on the application of an energy supply which, sooner or later, it must use universally.

REFERENCES

Conn, W. M. 1951. A solar furnace of 120 inches diameter for studying highly refractory substances. Rev. Sci. Inst., 22: 945–951.

Conference on the sun in the service of man. 1951. Proc. Amer. Acad. of Arts and Sciences, 79: 181–326.

Thermodynamics and Statistical Mechanics. *William P. Allis and Melvin A. Herlin.* International Series in Pure and Applied Physics. McGraw-Hill Book Company, Inc., New York, 1952. viii+239 pages. $6.00.

The avowed purpose of this text for seniors is that of stressing "the principles involved and their application to the properties of matter." The book presents a text readily understandable to students. The material is limited to typical and fundamentally important examples, and its many figures, tables, and problems are its chief merit. A more critical reader will not be quite satisfied with the presentation and formulation of the fundamental laws. The chapter on the first law explains that a quasistatic process AB is reversible (or irreversible) when the work done can be gained back completely (only incompletely) on the way back from B to A—without specifying the conditions (adiabatic ?) prevailing on the two ways. Next, the heat concept is based on the definition $dQ = C\,dT$, implying that one already knows what heat capacity is—after defining the latter by way of temperature differences levelling out, presuming that one has a temperature scale. Again: "Heat is therefore equivalent to irreversible work" (p. 67) and further: "When work is performed *reversibly* on a cycle then the quantity of work which appears is equal to the amount of heat that disappears, and vice versa." Such an introduction to the first law, often enough criticized by reviewers of elementary texts, is open to attack on the grounds of circularity of argument and lack of precision. Also, discussions about reversibility and irreversibility seem quite irrelevant for the first law and belong in the chapter on the second law. In the latter, the fundamental concept of absolute temperature is solely based on the equation of state of an ideal gas (p. 89), and with *this* T the entropy is defined, without even mentioning the pitfalls of this procedure. If the student, urged to look for information about the fundamental laws in some other modern textbook, will concentrate on the excellently written remaining parts of Allis-Herlin's book he will be able to learn a great deal about thermodynamics.

ALFRED LANDÉ.

Symposium on Radiobiology. *J. J. Nickson,* Editor. John Wiley & Sons, Inc., New York. 1952. xii+465 pp. $7.50.

This volume contains the 23 essays and principal discussions of the papers which were presented at the Symposium on Radiobiology held at Oberlin College, June 14–18, 1950, under the sponsorship of the National Research Council, the Atomic Energy Commission, and the Office of Naval Research. Because the essayists comprise a large part of the most active workers presently engaged in the investigation of radiobiological phenomena, the book is a landmark that constitutes an authoritative reference in this field of scientific endeavor.

The contents may be divided into the four principal topics of the symposium: (1) Fundamental physical concepts, (2) Chemical processes induced by the absorption of the energy of ionizing radiations, (3) Biochemical effects of ionizing radiations, and (4) Effects of radiation on living tissues.

Extensive bibliographies provide useful indices to the principal literature of the subjects with which many of the essays are concerned.

WM. G. MYERS.

R. H. BURTON COMPANY
can fill your optical needs

☆

BAUSCH & LOMB MICROSCOPES
Franchised Dealer
MICROSCOPE REPAIRING
. . . All Types
Authorized by American Optical Company
BINOCULAR REPAIRING
. . . All Makes
Authorized by Leading Manufacturers

BINOCULARS FOR SALE
AUTHORIZED DEALERS
D. P. BUSHNELL
and
BAUSCH & LOMB

Pick-up and Delivery Service
R. H. BURTON COMPANY
2504 Sullivant Avenue
COLUMBUS, OHIO
RAndolph 5472

CONSULT OUR
Advertisers

☆

PATRONIZE OUR
Advertisers

☆

MENTION
THE
OHIO JOURNAL
of SCIENCE

Now Ready . . .

A History of Entomology
By HERBERT OSBORN

A brief History of Entomology from ancient times down to the present day. Dr. Osborn, dean of entomologists, puts in type a most interesting story of entomology through all its various divisions. 255 photographs with sketches of many of the prominent entomologists of all time.

A book for the amateur, the teacher, the student.

$4.50 postpaid

THE SPAHR & GLENN CO.
FIFTY EAST BROAD STREET, COLUMBUS 15, OHIO